JOURNAL OF
SCIENTIFIC
&
INDUSTRIAL
RESEARCH

(Incorporating *Research and Industry*)

Compendium of Indian Medicinal Plants

4 Vols.

by R P Rastogi and B N Mehrotra

Vol.1 Reprinted with Addendum 1993. Pp515. Price Rs 300; Postage Rs 15.
Vol.2 Reprinted with Addendum 1993. Pp 859. Price Rs 550; Postage Rs 15.
Vol.3 1993. Pp 831. Price Rs 600; Postage Rs 15.
Vol.4 1995. Pp 930. Price Rs 750; Postage Rs 15.

The volumes provide information on all the compounds obtained from Indian plants that have medicinal properties. Chemical structures of these compounds break the monotony of the text. The isolation of these compounds from the plants and the description of their biological activities boost the usefulness of the compendium. The names of plants, families and orders of plants have been updated. Additional information in the volumes appears in the form of three indexes comprising local names, chemical constituents and biological activities. The first volume describes almost 1200 plants covering the ten year period 1960-69. The second volume covers the period 1970-79 and describes 1684 plants. The third volume covers the period 1980-84 and describes 1600 plants. The fourth volume covers the period 1985-89 and describes 1650 plants. The volumes include research done all over the world on medicinal plants found in India, whether indigenous or introduced. The volumes are useful for botanists, chemists and all those working on medicinal plants/natural products.

Order should be accompanied by Money Order/Demand Draft/IPO made payable to National Institute of Science Communication, New Delhi and sent to:
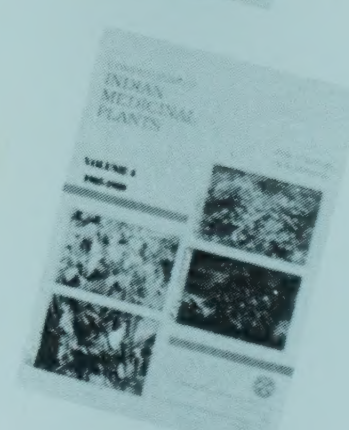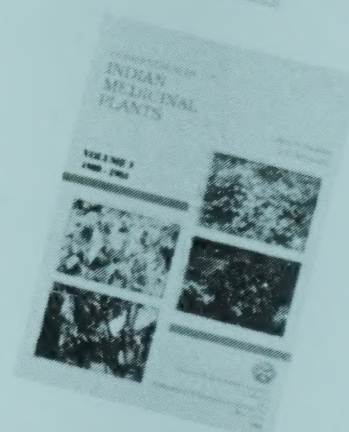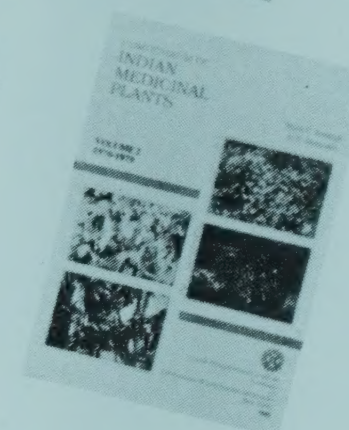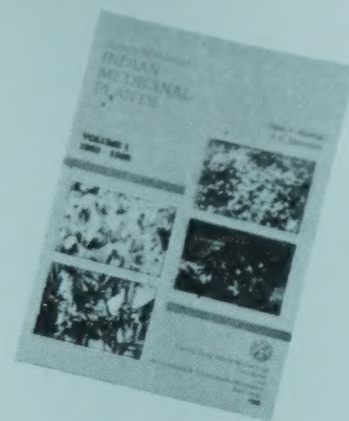
Sales and Distribution Officer

National Institute of Science Communication

Dr. K.S. Krishnan Marg, New Delhi-110012
Ph: 5785359, 5786301/7
Fax: 011-5787062, Telex: 031-77271

Journal of Scientific & Industrial Research

(Incorporating *Research and Industry*)

Editorial Board

The Journal of Scientific & Industrial Research is issued monthly. The Institute assumes no responsibility for the statements and opinions advanced by contributors. The editorial staff in their work of examining papers received for publication is assisted, in an honorary capacity, by a large number of distinguished scientists working in various parts of India and abroad.

Communications regarding contributions for publication in the journal and books for review should be addressed to the Editor, Journal of Scientific & Industrial Research, National Institute of Science Communication, Dr K S Krishnan Marg, New Delhi 110 012.

Correspondence regarding subscriptions and advertisements should be addressed to the Sales & Distribution Officer, National Institute of Science Communication, Dr K S Krishnan Marg, New Delhi 110 012.
Phone 5786301-07   Gram:PUBLIFORM   Telex:031-77271 PID IN

Annual Subscription
Rs 500.00 $ 200.00*   £ 125.00*

Single Copy
Rs 50.00* $ 20.00*   £ 15.00*

Payments in respect of subscriptions and advertisements may be sent by cheque, bank draft, money order or postal order marked payable to National Institute of Science Communication, Dr K S Krishnan Marg, New Delhi 110 012. Cheque/Demand draft may be drawn in favour of 'NATIONAL INSTITUTE OF SCIENCE COMMUNICATION, NEW DELHI'. Bank charges shall be borne by the subscriber; for inland/outstation cheques please add Rs 10.00 and for foreign cheques please add $ 2.00 or £ 1.00.

Supply of the journal will commence on receipt of subscription in advance.
*The rates of annual subscription and single copy include first class mail charges.
Claims for missing numbers of the journal will be allowed only if received within three months of the date of issue of the journal plus the time normally required for postal delivery of the journal and the claim.

CONTENTS

Review Papers

CONTENTS

Papers

CONTENTS

X-ray diffraction patterns of differently substituted cyanoethyl cellulose are recorded. The topography of fully substituted samples surface is explored using Scanning Electron Microscope. Variations found in the crystallographic parameters have been correlated with the degree of substitution.

Nahla A El-Wakil

Book Reviews

Sci-Tech Update

CONTENTS

Sci-Tech Update

- Plastics recycling process that does not discriminate
- Ethanol sensor measures beer's alcohol content online
- Bacteria communication
- Malaria's sticky killer protein discovered
- Human cells make perfect proteins
- Treatment for tough tumours
- New vaccines for urinary tract infections
- Failures in genetic testing found
- Sir John Maddox wins Cultural Award
- Rangaswamy Srinivasan to receive Esselen Award
- Report of the Working Groups of Information Society Forum of the European Commission
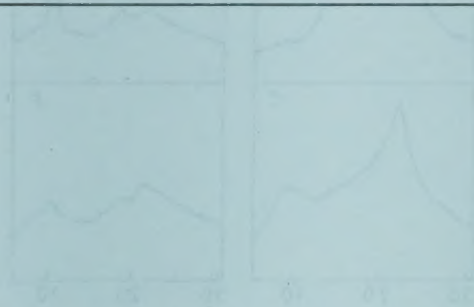
Chemistry of Terpinolene Oxide

Animesh Roy and K N Gurudutt[*]

Plantation Products, Spices and Flavour Technology Department, Central Food Technological Research
Institute, Mysore 570 013, India

Terpinolene oxide (1) belongs to the p-menthane group of monoterpenes and is easily derivable from the naturally abundant hydrocarbon, d-limonene (4). It is valuable as an intermediate for many aroma chemicals used in flavour and perfumery industry. Its chemistry is reviewed with special reference to the preparative methods of these compounds.

Terpinolene oxide (Scheme 1,1) is a tetra-substituted spiro- epoxide belonging to the p-menthane group of monoterpenes.[1] It was first reported in the oil of *Juniperus communis* and then from the essential oils of *Zanthoxylum piperitum* DC (Japanese pepper oil) and *Pastinaca sativa*. *P.sativa* is also a good source (~70per cent) of its parent hydrocarbon, terpinolene (2). Incidentally, many other essential oils have compound 2 as a constituent; notable among them is the oil from *Cupresus macrocarpa*. But, compound 2 is usually obtained by the acid-catalysed isomerisation of the more abundant terpenic hydrocarbon, dipentene (3), a by-product from pine oil, or from d-limonene (4), the major citrus terpene. Epoxidation of the tetra-substituted double bond in compound 2 is achieved with organic peroxy acids under controlled conditions.[2]

According to a procedure standardised in authors' laboratory,[2] compound 2 is formed to an extent of 35 to 40 per cent , along with isomeric hydrocarbons,*viz*. compound 3 and 5, when compound 4 is gently refluxed under stirring with 0.2 part by weight of activated silica gel (100 to 200 mesh) for about 2 h (Scheme 1). Fractionation of this mixture to obtain pure compound 2 is rather tedious and time consuming. Alternatively, the mixture on treatment with 40 per cent peracetic acid at -20°C in amounts equivalent to the terpinolene content, followed by a simple work-up and easy fractionation affords compound 1. Its physical properties are given in Fig. 1.

Compound 1 is recognized as an useful synthetic intermediate for many aroma chemicals. The inherent polarity and strain of the three-membered oxide ring, (oxiran group), make it susceptible to many chemical transformations, often attended with skeletal rearrangements. But, reduction of the oxiran is difficult due to its unfavourable stereochemistry. In fact, on catalytic hydrogenation over platinum dioxide, only the cyclohexene ring is reduced, yielding
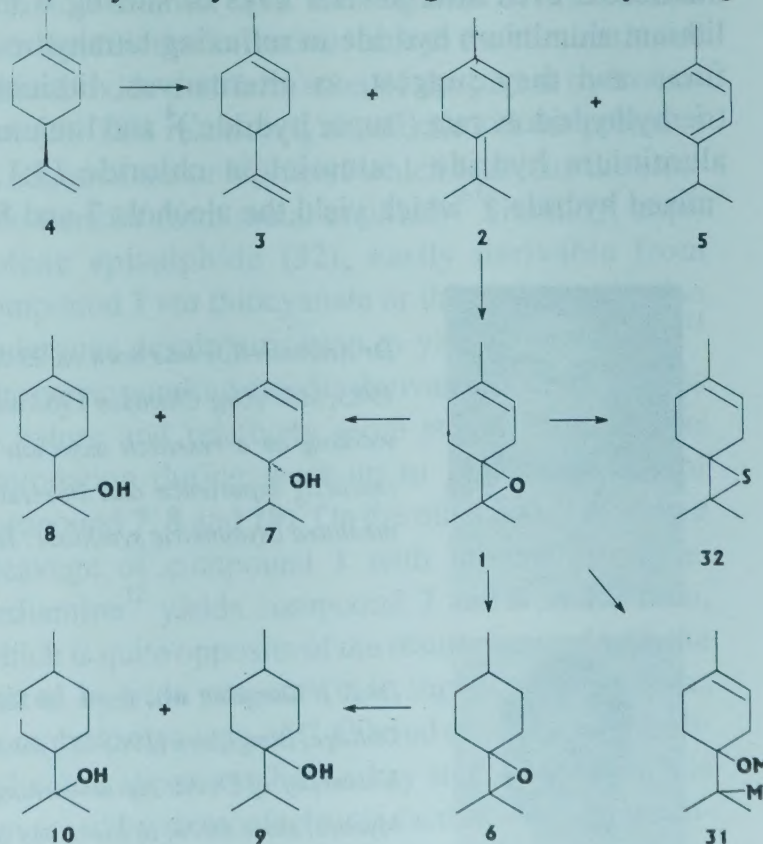
Scheme 1 — Preparation of terpinolene oxide (1) and its derivatives

---

*Author for correspondence
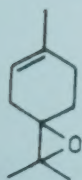
Terpinolene oxide   Appearance : Colourless liquid

p-Menth-1-en-4(8)-oxide   b. p. 64.5 - 65.5 ^{0} C / 2 Torr

2,2,6-Trimethyl-1-oxa-spira [2.5] oct-5-ene

Ref. index : 1.4703 at 22 ^{0} C

CAS Registry Number : 4584-23-0   Sp. Gr. : 0.935 at 22 ^{0} C

Fig. 1 — Physical properties of terpinolene oxide (1)

p-menthane-4,8-oxide (**6**).[3] Approach of the hydride transferring reagents is also expected to be difficult. But there are conflicting reports on the lithium aluminium hydride reduction of compound **1**.[3] Employment of several-fold excess of the hydride in the reaction is reported to give a mixture of isomeric alcohols, *viz.* 4-terpinenol (**7**) and α-terpineol (**8**) in about 50 to 74 per cent yield. On the other hand, two other groups of workers[3,4] report that compound **1** is unaffected even after several days of stirring with lithium aluminium hydride in refluxing tetrahydrofuran and they suggest, as alternatives, lithium triethylhydridoborate ('super hydride')[4] and lithium aluminium hydride : aluminium chloride (3:1, 'mixed hydride')[3] which yield the alcohols **7** and **8**

in the ratio 4.5 : 1 and 3:1 respectively. (Similarly, compound **6** affords a 3:1 mixture of the alcohols **9** and **10**).[3] Although the former reagent affords higher amounts of compound **7** and **9**, the latter is relatively less expensive and hence useful for large scale preparations. The regioselective ring opening leading to the predominant formation of compound **7** and **9** in these reactions could be attributed to the preferential attack of the hydride ion on the less hindered carbon (C-8) and concomitant release of strain in the molecule. These isomeric alcohols can be separated easily by efficient fractional distillation using packed columns. While α-terpineol (**8**) is commercially made by direct hydration of α-pinene or dipentene, compound **7** is usually derived from compound **1** by the following indirect routes.[2]

The oxiran group in compound **1** is cleaved with diethylamine to give an amino alcohol (**11**) in 45 per cent yield, which on heating with hydrogen peroxide and methanol affords *p*-mentha-1,8-dien-4-ol (**12**).

Compound **12** is also formed in about 53 per cent yield when compound **1** is isomerised in the presence of *p* -toluenesulphonic acid in benzene around 30°C. Alternatively, it is obtained in 60 per cent yield by the photochemical oxidation[5] of compound **2** into a hydroperoxide followed by reduction with sodium sulphite. Catalytic hydrogenation of compound **12** over Raney nickel in methanol at 40°C affords compound **7** in nearly quantitative yield.[2]

A detailed study[6] of the reactions of compound **1** with various Bronsted and Lewis acids indicates that catalyst, solvent and temperature have profound ef-

Dr Animesh Roy was born on 23 January 1962, in Siliguri, West Bengal. He obtained BSc Honours in 1983, MSc (Org Chem) in 1985 and PhD in 1991 from the University of North Bengal. He is presently working as a research associate at Central Food Technological Research Institute, Mysore. His research experience and interest include natural products, chemical transformation and enzyme mediated asymmetric synthesis . He has seven papers to his credit.
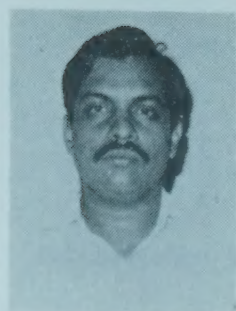
Dr K N Gurudutt was born on 24 March 1949, in Shimoga, Karnataka State. He studied in Central College, Bangalore (1965-70) for his BSc (Hons) and MSc degrees. He obtained his PhD in 1975 from University of Delhi. He is working as a scientist at Central Food Technological Research Institute, Mysore, since 1976, in the areas of flavour chemistry, bio-active natural products, organic synthesis and chemical process development. He has 32 research papers and eight patents to his credit.

fect on the nature and the composition of products. The various chemical transformations observed in these reactions are summerised in Scheme 2. As reported earlier[5], compound 12 is the major product (>70 per cent) of the reaction of compound 1 with p-toluene sulphonic acid in ether or acetone medium at ambient temperature; but, p -cymene (13) is predominantly formed in refluxing benzene. Similarly, with other protic acids and at higher temperatures, initially formed compound 12 as well as its isomers, p-mentha-1,3-dien-8-ol (14) and p-mentha-1,4-dien-8-ol (15) undergo dehydration to yield p- mentha-1,3,8(9)-triene (16) and p-mentha-1,4,8(9)-triene (17), both of which further undergo isomerisation or / and aromatisation to afford compound 13 and dehydro-p-cymene (18). Alternatively, compound 14 and 15 may get aromatised to yield p- cymen-8-ol (19) and thence compound 18.

In the presence of Lewis acids, seven-membered ketones (ring expansion products) are formed as the main products. Zinc bromide in diethyl ether is particularly useful in effecting the transformation of compound 1 into karahanaenone (20) and isokarahanaenone (21). Authors found that lithium perchlorate in benzene at 50°C and anhydrous magnesium bromide in ether at 27°C also brought about this transformation. The reaction of compound 1 with borontrifluoride etherate in refluxing ether is very slow but it furnishes, besides the aforesaid isomerised products and hydrocarbons, 8-fluoro-p-menth-1-en-4-ol (22) in 12 per cent yield. In contrast, the reaction of compound 1 with borontrifluoride etherate or perchloric acid in acetone is extremely fast, at even sub-ambient temperatures and afford p-menth-1-en-4,8-dioxy dimethyl acetal (23) (dioxolan derivative). Thus, a series of dioxolan derivatives (23-27) have been prepared by reacting compound 1 with aldehydes and ketones containing 1 to 4 carbon atoms.

The oxiran ring of compound 1 is opened by protic solvents in the presence of acid to give predominantly 8-substituted p-menth-1-en- 4-ol derivatives. (Scheme 2, compounds 11, 22, 28, 29 and 30). When contacted with dilute sulphuric acid, compound 1 gives the diol (28) and with dry hydrogen chloride at –15°C[7], affords the chlorohydrin (29). Authors found that the reaction of compound 1 with glacial acetic acid in the presence of anhydrous sodium acetate (10

per cent w/w) at 100 °C for 4 h yielded a 5:1 mixture of hydroxyacetates, of which compound 30 was major (the ratio was determined by the integration of acetoxyl signals at δ 1.95 and 2.00 in ^{1}H NMR of the product).

In contrast to its high reactivity towards acids, compound 1 is normally resistant to bases. However, it isomerises in the presence of aluminium isopropoxide, under forcing conditions, mainly to compound 12.[6] On the other hand, with non-nucleophilic and bulky bases like potassium t-butoxide[8], it affords compound 14 and 15 as the major products. While the latter could be isolated in pure form by column chromatography, the former is detectable only by GC-MS analysis. Here, β-elimination of hydrogen occurs from the methylene groups of the strained cyclohexene system, leading to the primary products which readily aromatise to compound 19, as observed in the reaction of compound 1 with N- lithio-ethylenediamide.

The reactions of compound 1 with lithium and sodium in aprotic solvents (e.g. diethyl ether and tetrahydrofuran) initially takes identical course.[9] Transfer of an electron from metal to the oxiran results in the predominant formation of a radical anion which further reacts with another metal atom to yield a dianion (31). Prolongation of the reaction with the dilithio derivative leads to the elimination of lithium oxide and formation of the parent hydrocarbon (2). This reaction is accelerated in the presence of naphthalene or biphenyl which facilitate the electron transfer from metal to oxide.[10] Similarly, terpinolene episulphide (32), easily derivable from compound 1 via thiocyanate or thiuronium salt, also undergoes desulphurisation to yield compound 2.[11] The corresponding disodio derivative formed is ionic in nature and relatively more stable. It undergoes protonation during work-up to give a mixture of compound 7, 8 and 19.[9] On the other hand, reductive cleavage of compound 1 with lithium in ethylenediamine[12] yields compound 7 and 8 in 1:2 ratio, which is quite opposite of the result obtained with the mixed hydride reagent (vide supra). In this case, homolytic cleavage of C-O bond to yield stable radical anion appears to be the key step — a step that is governed by stereoelectronic factors — in determining the composition and constitution of the product. The reaction of compound 6 with lithium in ethyle-

11. X = NMe₂
22.   = F
28.   = OH
29.   = Cl
30.   = OAc

23. R = R¹ = Me
24. R = Me ; R¹ = H
25. R = Et ; R¹ = H
26. R = Iso-Pr; R¹ = H
27. R = Et ; R¹ = Me
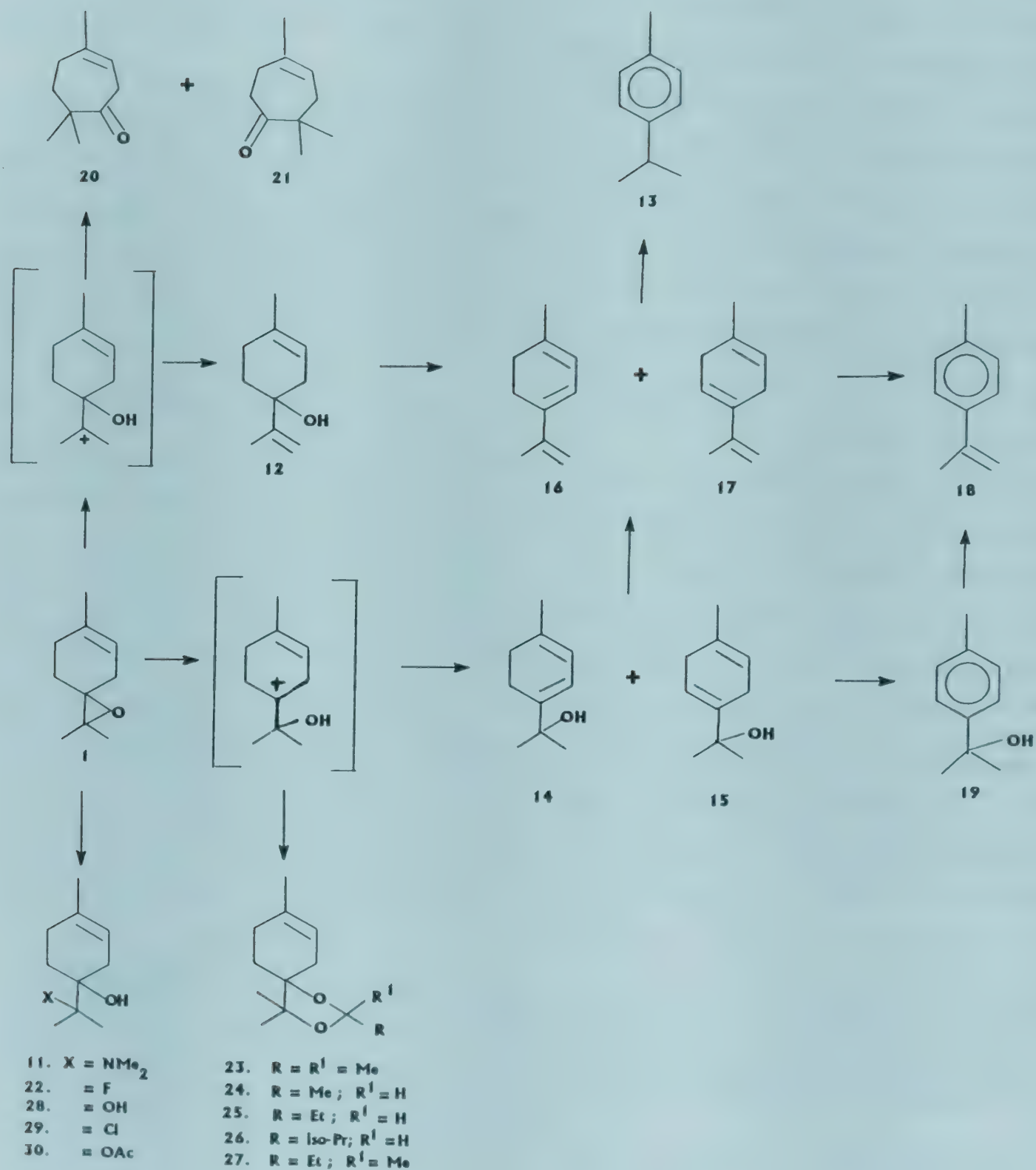
Scheme 2 — Chemical transformations of terpinolene oxide (1)

nediamine follows similar course leading to almost exclusive formation of compound **10**.[12]

Conclusions

Easy accessibility from the naturally abundant monoterpene, *d-* limonene (or dipentene) and high reactivity towards a variety of reagents make terpinolene oxide (**1**) an excellent synthetic intermediate for several aroma chemicals and other useful products. The most important commercial use of terpinolene oxide (**1**), apart from itself being an aroma chemical, is in the synthesis of 4-terpineol (**7**), a prized flavourant. The other aromatic alcohols derivable from it are, α-terpineol (**8**), *p*-cymene-8-ol (**19**), 4-hydroxylimonene (**12**) and *p*-mentha-1,4-dien-8-ol (**15**). 1,3-Dioxolan derivatives of compound **1** (**23** - **27**) have mild but tenacious aroma and exhibit fixative property. Further, compound **1** gives access to the seven-membered ketones, karahanaenone (**20**) and isokarahanaenone (**21**), which are constituents of 'oil of hop'. It has also been employed as starting material for the synthesis of γ-bisabolene[13] and cinmethylen[7], a novel 1,4-cineol herbicide.

References

1   *Handbook of Terpenoids*, **Vol. 3**, edited by Sukh Dev (CRC Press, Boca Raton, Florida) 1982, pp 291 and references cited therein.

2   Ravindranath B, *J Sci Ind Res*, **42** (1983) 82 and references cited therein; *Chem Abstr*, **98** (1983) 217540 j.

3   Gurudutt K N & Ravindranath B, *Synthesis*, (1983) 888.

4   Cocker W & Grayson D H, *J Chem Soc Perkins Transl*, (1978) 155.

5   Klein E, *Ger Offen*, 1, 235, 306 (1967); *Chem Abstr*, **67** (1967) 64379 m.

6   Gurudutt K N, Pasha M A & Ravindranath B, *Indian J Chem*, **24B** (1985) 820 and references cited therein.

7   Lee P W, Stearns S M, Powel W R, Stoutamire D W, Payne G B, Woodward M D, Woodward W B, Silveira E J & Ehmann A, *J Agric Food Chem*, **34** (1986) 162.

8   Roy A, Gurudutt K N & Rao S, *Indian J Chem*, **34B** (1995) 636.

9   Gurudutt K N, Pasha M A, Ravindranath B & Srinivas P, *Tetrahedron*, **40** (1984) 1629.

10   Pasha M A and Ravindranath B, *Indian J Chem*, **22B** (1983) 1149.

11   Rajanikanth B & Ravindranath B, *Indian J Chem*, **23B** (1984) 879.

12   Gurudutt K N, Rao S & Shaw A K, *Indian J Chem*, **30B** (1991) 345.

13   *The Total Synthesis of Natural Products*, **Vol. 5**, edited by J ApSimon (John Wiley & Sons, New York) 1983, pp 47.

Inorganic Membranes: New Materials for Separation Technology

A Prakash Rao, N V Desai and R Rangarajan

Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India

New developments in inorganic membrane technology have been revolutionizing the chemical industry in recent times. While acting as substitutes for polymeric membranes, inorganic membranes are also experiencing increasing usage in applications where traditional materials are inappropriate. Ceramic-based inorganic membranes are widely preferred in situations where polymeric membranes cannot be used such as at very high temperatures and pH extremes which allows sterilization of process equipments for food and pharmaceutical applications. Inorganic membranes have applications in chemical, environmental, food, and pharmaceutical industry sectors. Major industrial applications include chemical process/solvent cleanup, catalyst recovery, hydrocarbon-related uses, reactors, gas/gas separations and other analytical uses. Environmental applications for inorganic membranes include water treatment, treatment of waste streams, and gas cleanup. Although alumina is currently the dominant type of ceramic material used in inorganic membranes, other types of inorganic membranes are also being developed which include new hybrid membranes and metallic membranes such as stainless steel, silver, and palladium. Thus, it is clear that lucrative opportunities exist in the rapidly evolving market for inorganic membranes.

Information

In the past few years a number of research papers have been published concerning the preparation and characterization of inorganic membranes[1-8]. Subsequently, there has been a growing interest in utilizing these inorganic membranes to address a variety of separation problems in many industries[9-14]. Various inorganic membranes made from metals, inorganic polymers and ceramics have been proposed for liquid and gas separation applications[12-15]. The interest in utilizing such membranes in separations has increased since the advent of consistent-quality commercially available ceramic membranes with narrow pore size distributions. Inorganic membranes exhibit unique physical and chemical properties that are only partially shown or not shown at all by organic membranes. For example, they can be used at significantly higher temperatures, have better structural stability without the problems of swelling or compaction, generally can withstand more harsh chemical environments, are not subjected to microbiological attack and can be backflushed, steam sterilized or autoclaved.

Classification

Inorganic membranes can be classified into the following groups.

- Ceramic membranes such as alumina, silver or titania.
- Zirconia membranes.
- Palladium based membranes.
- Glass membranes.
- Metal membranes such as stainless steel or silver.

Ceramic membranes are highly porous (pore diam >0.1 μm) and are characterized by high permeability and low selectivity. Due to their high porosity they have been used for ultrafiltration and microfiltration applications and also used as supports for developing thin films to produce composite membranes for nanofiltration separations[10,11,16-18]. Among the ceramic membranes, alumina is currently the most dominant material used and is gaining acceptance for liquid phase separations. Alumina membranes for liquid phase separations came to commercial fruition from uranium isotope enrichment work.[19-22]

Zirconia and palladium-based membranes are dense in nature and have shown to be permeable only to certain gases (e.g, Hydrogen and Oxygen). These membranes have high selectivity but low permeability and have been used for H_2/O_2 separation and polyvinyl - alcohol recovery as a sizing chemical for the textile industry. These materials are also used in sensors, electrodes and coatings[23]. Stabilized zirconia is frequently used as electrochemical oxygen sensor for monitoring combustion products from boilers and kilns or automobile exhaust.

The properties of glass membranes are in between to those of alumina and zirconia membranes. However,in many applications, glass membranes are surface modified or feed stream is pretreated with a chemical such as aluminium chloride to retard the silica dissolution from glass in aqueous solutions. Glass membranes have been commercially used for bacteria removal, blood filtration and fractionation[23]. However,until recently,they have not been marketed widely as membranes.

Porous metal membranes have long been commercially used for particulate filtration and in some cases for microfiltration applications involving harsh environments[23]. They have also been used for blood analysis and production of ultrapure water.

Literature survey on inorganic membranes indicates that 80 per cent of the papers published are devoted to ceramic membranes alone which means that amongst all inorganic membranes, ceramic membranes are widely preferred in separation applications because of their maximum thermal stability and other special advantages which are spelt below. Hence, the paper is restricted to the details regarding properties and characteristics of ceramic membranes.

Advantages of Ceramic Membranes

The special features which ceramic membranes enjoy are :

(i)   *Good Chemical Stability* — Ceramic membranes can withstand organic solvents, chlorine and pH extremes.They can also withstand appreciable chemical attack,particularly when exposed only periodically to strong acids or bases.

(ii) High Temperature Applications — Ceramic membranes are stable up to very high temperatures (1000 °C),allowing sterilization of process equipment for food and pharmaceutical applications.

(iii) *Stability to microbial degradation.*

(iv) *Good Mechanical Stability* — In general, ceramics are hard and resistant to abrasion.

(v)   *Easier Cleaning Conditions* — Ceramic membranes can be back- flushed to provide periodic regeneration of the membrane to restore back the permeability lost due to fouling. These membranes can also be steam sterilized and chemically cleaned with caustic soda followed by nitric acid in the temperature range of 50-80°C.

UF and MF Applications of Ceramic Membranes

• Concentration of whole or skimmed milk.
• Clarification of fruit juices.
• Microfiltration of industrial and municipal water.
• Sterilization of liquids for pharmaceutical industry.
• Cell harvesting and sterilization in biotechnology.
• Oil-water separation.
• Concentration of dilute latex waste water.

Ceramic Nanofiltration Membranes

Until recently, ceramic membranes were characterized and classified as falling into either the microfiltration or the ultrafiltration range. But now, some initial examples have appeared wherein partial rejections of low molecular weight solutes have been achieved which are characteristic of nanofiltration separations.

Composite membranes having heteropolysiloxanes deposited on microporous ceramic substrates were prepared which gave solute rejections of 10-20 per cent for NaCl, 50 per cent for sucrose and 100 per cent for acid yellow 42 dye (mol wt 749)[24]. Other applications of ceramic nanofiltration membranes also include dye rejections like acid orange dye (mol.wt.493) and solute rejections like sodium sulfate, o-phenanthroline and sucrose[25]. Vitamin B_{12} rejections of up to 100 per cent were also obtained using SiO_2-Al_2O_3 ceramic composite membranes.

Dynamic Membranes or Salt-rejecting Membranes

Recently, another class of ceramic membranes has emerged wherein ceramics are used as porous supports for depositing oxide films to produce ultrathin composite membranes. For example, graphitic oxide ultrathin membranes deposited as multilayers on to porous supports by suction filtration techniques, exhibited salt rejections of up to 94 per cent with 0.5 per cent NaCl solutions (0.5-1.0 gfd flux at 600 psig)[26]. Best results were obtained for six-layer deposits, total deposit thickness being 0.3-0.4 um . A breakthrough in terms of high water flux combined with nanofiltration rejection characteristics was achieved for dynamic membranes[27] formed with hydrous zirconium (1V) oxide wherein NaCl rejections of up to 77 per cent were obtained for very dilute salt solutions. However, none of the dynamic membranes so far have yielded performance data worthy of commercial development.

Characteristics of Commercial Ceramic Membranes

Due to their inherent stability, sensors based on ceramic membranes are being widely studied and used in some cases for high temperature applications for sensing the presence of gases or chemicals for analytical purposes. Stabilized zirconia is frequently used as an electrochemical oxygen sensor for monitoring combustion products from boilers and kilns (350- 600°C) or automobile exhaust (350-900°C). Other inorganic sensors include palladium/ silver alloy for hydrogen (pH) sensing, sodium containing glass for sodium sensing, chalcogenide glasses for the detection of copper, heavy metals and bromide ions and anodized alumina in enzyme sensors. It should be noted that, in addition to thermal stability, ceramic membranes as sensors may be advantageous in their durability over polymeric membranes for repeated contacts.

Another potential application of the commercial porous inorganic membrane materials lies in the area of liquid membranes where the solid porous matrices (solid membranes) are used as supports for some liquid separation carriers.

Although the use of inorganic membranes as separators for catalytic reactions is at the developing stage, the potentials of membrane reactors for improving yield and selectivity and for integrating two unit operations, reaction and separation, into one are already recognized. It has been proved experimentally that the continuous removal of a product or products from a reaction mixture through an inorganic membrane can significantly increase the conversion by displacing the reaction equilibrium towards the product side, and in some cases, enhance the selectivity by suppressing undesirable side reactions. Controlled addition of a second membrane-selective reactant through an inorganic membrane also resulted in improved conversion and selectivity while providing safer operating environment.

Most of the reported studies on inorganic membrane reactors have been on hydrogenation-dehydrogenation, dehydration and decomposition reactions as exhaustively reviewed by H P Hsieh in AIChE symposium series[5].

Routes of Production

There are two main methods of making ceramic membranes namely :

(i) Suspended powder or particles suspension technique which leads to the development of MF membranes having 100 nm to 10 μm pore diam.

(ii) Sol-gel techniques which permit UF membranes to be obtained (1-100 nm pore diam).

If one goes through the literature, he will find that these two techniques are most commonly employed[8,15,28-30] to generate either MF or UF membranes. Figure 1 gives the simple description of the two most common routes by which ceramic membranes can be obtained.

However, in recent times new techniques have emerged[31] to produce a different class of inorganic membranes such as (iii)Suction filtration technique wherein ultrathin membranes are deposited as multilayers on to porous supports, and (iv) Combustion chemical vapor deposition technique which permits thin oxide films to be obtained or deposited on a porous substrate. Shortly termed as CCVD, the technique combines features of chemical vapor deposition and thermal spraying.

Characterization of Ceramic Membranes

The methods most commonly employed for the characterization of ceramic membranes are (i) Mercury porosimetry, (ii) Coulter porosimetry, and (iii) Permeation tests[29,32,33].

Two Ways To Obtain Inorganic Membranes

SUSPENDED POWDER TECHNIQUE   SOL-GEL TECHNIQUE

Inorganic Powder   Metal Alkoxides

 solvent adding   controlled hydrolysis

Suspension   Sol

 inorganic binders + coating   inorganic binders + coating

Thin Layer   Sol Layer

 drying   drying

Dried Thin Layer   Gel Layer

INORGANIC MEMBRANES
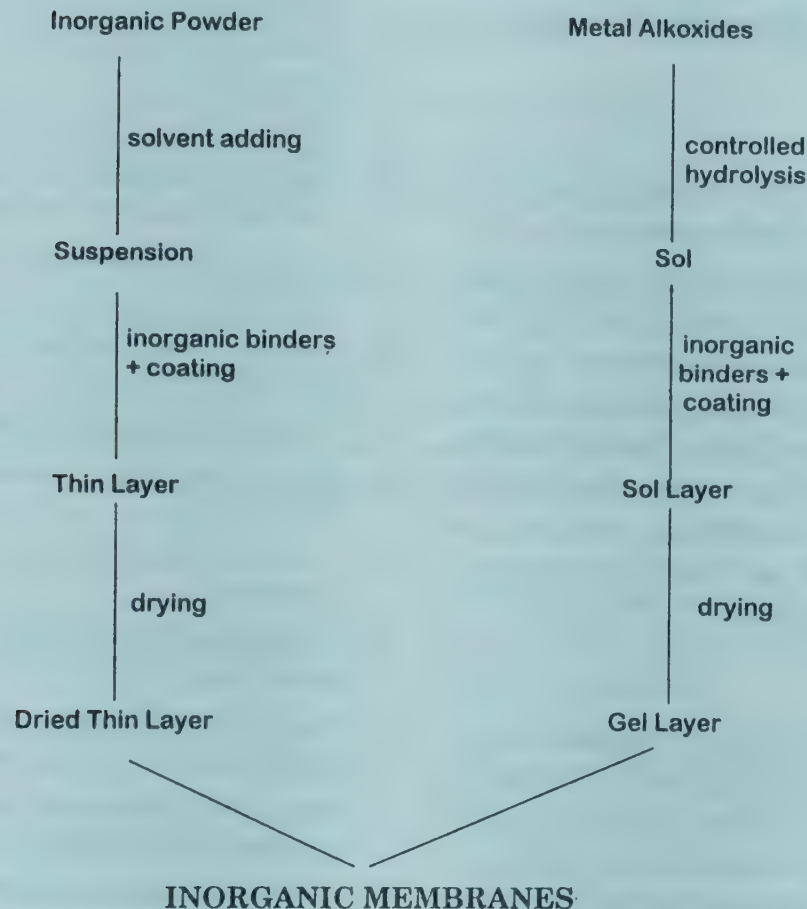
Fig.1 — Schematic representation of the two probable ways or routes by which inorganic membranes can be obtained

Mercury porosimetry is frequently used for the characterization of the pore structure of solid materials. This method is based on the measurement of the mercury uptake into the previously evacuated porous material under increasing pressure of mercury. Coulter porosimetry is a relatively new method for the characterization of special porous materials. This method is based on two physical phenomena: Capillary forces in pores filled with liquids and the gas flow through empty cylindrical pores. The permeation method is based on the measurement of the dependency of the gas flow rate on pressure differences across the membrane. Measured data enable the determination of the mean pore radius and its number in a membrane sample.

Major Hurdles and Challenges for Ceramic Membranes

The major drawbacks faced by these membranes are:

- Their uncompetitively high cost of production compared to that of polymeric membranes.
- Their wider MWCO limits - to produce ceramic UF membranes with retention properties comparable to those of the lowest MWCO polymeric membranes is a big challenge.
- Their lower water fluxes — Currently available ceramic UF membranes have low water flux which can limit the process economics. Also, water permeabilities for the equivalent porous polymeric membranes are typically at least five times higher.

- In most of the applications, the operating temperature is limited to 150 °C due to the limitations of the sealing and packing materials used presently. Hence there is a need to develop sealing and packing materials that can withstand higher temperatures so that the thermal stability of ceramic membranes can be fully exploited.

Market Opportunities

Rather than strictly acting as replacements for polymeric membranes, inorganic membranes are experiencing increasing usage in applications where traditional materials are inadequate. Over the next ten years, inorganic separation membranes are expected to account for about 15 per cent of total membrane module sales worldwide. Presently, membranes composed of ceramics account for about 69 per cent of all inorganic membranes sold and are expected to account for 86 per cent of all inorganic membrane sales by the year 2005.

Conclusions

New developments in inorganic membrane technology have been revolutionizing various industries in recent times. While the next few years are expected to see numerous advances in the field of membrane separations, inorganic membranes are sure to experience rising demand especially in situations where polymeric membranes cannot be used. Inorganic membranes have applications in chemical, environmental, food and pharmaceutical industry sectors. It is very clear that lucrative opportunities exist in the rapidly evolving market for inorganic membranes.

References

1   Bottino A, Capanneli G, Grosso A, Monticelli, Cavalleri O, Rolandi R & Soria R, *J Memb Sci*, 95 (1994) 289.

2   Jia M D, Peinemann K V & Behling R D, *J Memb Sci*, 82 (1993) 15.

3   Jia M D, Peinemann K V & Behling R D, *J Memb Sci*, 73 (1992) 119.

4   Hwang S T & Li D, *J Memb Sci*, 59 (1991) 331.

5   Hsieh H P, Bhave R R & Fleming H L, *Inorganic Membranes, AIChE Symp Ser*, 84 (1988) 1.

6   Leenars A F M, Keizer K & Burggraaf A J, *J Mater Sci*, 19 (1984) 1077.

7   Hackley V A & Anderson M A, *J Memb Sci*, 70 (1992) 41.

8   Keizer K, de Lange R S A, Hekking J H A & Burggraaf A J, *J Memb Sci*, 99 (1995) 57.

9   Mikulasek P & Cakl J, *Desalination*, 95 (1994) 211.

10 Aimar P, Taddei C, Lafaille J P & Sanchez V, *J Memb Sci*, 38 (1988) 203.

11 Komoto M, Kishihara S, Tamaki H, & Fujii S, *J Memb Sci*, 41 (1989) 103.

12 Sperry D P, Falconer J L & Noble R D, *J Memb Sci*, 60 (1991) 185.

13 Huang R Y M & Feng X, *J Memb Sci*, 74 (1992) 171.

14 Sano T, Yanagishita H, Kiyozumi Y, Mizukami F & Haraya K, *J Memb Sci*, 95 (1994) 221.

15 Morooka S, Kusakabe K & Ichiki K, *J Memb Sci*, 95 (1994) 171.

16 Murase T, Pradistsuwana C, Iritani E & Kano K, *J Memb Sci*, 62 (1991) 187.

17 Elmaleh S & Naceur W, *J Memb Sci*, 66 (1992) 227.

18 Lin Y S, Jayaraman V, Pakala M & Lin R Y, *J Memb Sci*, 99 (1995) 89.

19 Hsieh H P, Bhave R R & Fleming H L, *J Memb Sci*, 39 (1988) 221.

20 Anderson M A, Gieselmann M J & Xu Q, *J Memb Sci*, 39 (1988) 243.

21 Burggraaf A J, Uhlhorn R J R & Keizer K, *Chemtech*, (1986) 560.

22 Burggraaf A J, Keizer K, Uhlhorn R J R & Vuren R J V, *J Memb Sci*, 39 (1988) 285.

23 Hsieh H P, *Inorganic Membranes, AIChE Symp Ser*, 85 (1989) 53.

24 Guizard C, Larbot A & Cot L, *Proc Int Conf Inorg Memb, Montpellier*, 3-6 July 1990, p. 55.

25 Larbot A, Alami-Younsi S, Persin M, Serrazin J & Cot L, Alumina Nonfiltration Membrane, Paper presented at *Fifth Annu Meet North Amer Memb Soc, Lexington*, 17-20 May 1992.

26 Flowers L C, Lee P K, Bober E S, Gjertsen M H & Berg D, *Graphitic Oxide Containing Reverse Osmosis Membranes*, NTIS Report No PB - 203843, *loc cit*, April 1969.

27 Shor A J, Kraus K A, Smith W T & Johnson J S, *J Phys Chem*, 72 (1968) 2200.

28 Okubo T, Watanabe M, Kusakabe K & Morooka S, *J Mater Sci*, 25 (1990) 4822.

29 Larbot A, Fabre J P, Guizard C & Cot L, *J Memb Sci*, 39 (1988) 203.

30 Klein L C & Gallagher A, *J Memb Sci*, 39 (1988) 213.

31 Gavalas G R & Tsapatsis M, *AIChE J*, 38 (1992) 847.

32 Rocek J, Uchytil P, *J Memb Sci*, 89 (1994) 119.

33 Batchu H R, Venkataraman K, Choate W T, Torre E R & Husung R D, *J Memb Sci*, 39 (1988) 259.

Physico-chemical Adsorption Treatments for Minimization of Heavy Metal Contents in Water and Wastewaters

Ali Mohammad* and Mohamed Najar PA

Department of Applied Chemistry, Z H College of Engineering & Technology, Aligarh Muslim University, Aligarh 202 002, India

An attempt has been made to compile various techniques and materials used for the adsorption treatment of water and wastewater for minimization/removal of heavy metal contents. One hundred four references have been cited from the literature to cover the work done during 1991 till the end of 96. Various adsorbents have been employed for effective removal of toxic metals. Treatment methods, viz. by chemical precipitation/co-precipitation, membrane filtration, ion-exchange have been used along with adsorption. New adsorbent materials have also been recommended for the effective treatment of natural and wastewaters.

Introduction

Lot of work dealing with environmental pollution and control is available, but most of the information is scattered through many scientific and technical journals and comparatively few books on the subject have come into light. It is easy to describe environmental pollution in a more precise way as the 'unfavourable alteration of our surroundings' and which is created by humans. Rapid industrialization and urbanization result in the deterioration of air, water, and land quality. Various pollutants are produced by present humans and many of these reach the aquatic system either directly or indirectly. This is specially true of heavy metals because it is not ameliorated by natural phenomena of biochemical decomposition. However, it can be attenuated by adsorption on a suitable medium and recovered or isolated through various treatment techniques.

Most of the heavy metals, except iron and manganese and sometimes arsenic are due to the anthropogenic activities. High concentration of heavy metals in surface water is generally associated with industrial discharges[1]. Metals containing industrial effluents constitute a major source of metallic pollution of the hydrosphere. The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic

substances in aquatic environment. The metals are of special concern because they are non-degradable and therefore persistent.

Among the various methods described, adsorption is generally preferred for the treatment of polluted water due to its high efficiency, easy handling, availability of different adsorbents and cost-effectiveness. The extent of adsorption is largely dependent on the physicochemical properties of the adsorbent such as surface area, particle size, porosity, residual charges on the adsorbent and adsorbate such as electric charge, capacity for aggregation of the degree of dissociation, solubilization, and ionization. In addition, nature of solvent, concentration, temperature, pH, the presence of foreign ions, etc., greatly influence the range of adsorption. The adsorption studies are significant both theoretically and practically as they can be utilized in the detection, determination and treatment of inorganic and organic pollutants including pesticides. The use of adsorption processes for the removal of pollutants by the use of solid adsorbents has been considerably studied recently.

Activated carbon has been used by many investigators as an effective adsorbent for removing organic and inorganic contaminants from water, wastewater, and air samples[2]. However, its use poses an economic problem and hinders large scale use for the reduction of heavy metal pollution in the developing countries.

*For correspondence

Several alternative adsorbents which have been proved quite useful due to their low cost and wide availability include fly ash[3], peat[4], fibrous keratinous material such as wool and hair[5,6], clays[7], alumina bauxite[8], suspended particles of river water[9], sludge[10], agricultural wastes, polymerized onion skin with formaldehyde[11], EDTA modified cellulose materials[12], modified barks[13], plain barks[14], barley straw[15], low rank coal[16], peat moss[17], fertilizer slurry[18], waste tyre rubber[19] and tea leaves[20]. In wastewater treatment, the process of adsorption has found improved application over other methods due to its clean sludge free operation.

The information regarding the various adsorbent used by workers for monitoring and removing heavy metals from water and wastewaters has been encapsulated in Table 1.

Adsorbents used for the removal of some toxic metals from water and wastewaters include: acid soils (A_1), activated carbon (A_2), Amberlite XAD - 8 (A_3), Amberlite IR - 120 (A_4), banana pith (A_5), bentonite clay minerals (A_6), bismuth trioxide (A_7), blast furnace flue dust (A_8), blast furnace sludge/(gas cleaning) (A_9), bottom ash (A_{10}), burnt clay and soils (C-black) (A_{11}), calcareous soils (A_{12}), carboxylic ion-exhange (A_{13}), Ca-alginate and *C. Vulgaris* (a green algae) *Z-ramigera* (an activated sludge bacterium), *S-cerevisiae* (a yeast), cells immobilized on Ca-alginate (A_{14}), canola meals (A_{15}), charcoal (A_{16}), chattonella antique (A_{17}), China clay (A_{18}), chromate waste (A_{19}), clay minerals (A_{20}), coal based adsorbents (A_{21}), cocoa growing soils (A_{22}), coconut shell carbon (A_{23}), coconut fibre compost (A_{24}), colloidal iron (III) hydroxide (A_{15}), commercial green tea (A26), compost (A27), corncob (A28), fly ash (A_{29}), geothite (A_{30}), granular activated carbon (A_{31}), granular peat (A_{32}), granules consisting foamed clay, Fe, and lime (A_{33}), hydrous oxide (A_{34}), hydroxy apatite (A_{35}), illicit soils (A_{36}). Inactivated cells of Mueor rouxii (A_{37}), ion-exchange Duolite (A_{38}), ion exchange resin (A_{39}), iron oxide coated granular activated carbon (A_{40}), laterite minerals (A_{41}), lobster chitosan (A_{42}), modified activated carbon (A_{43}), moss peat (A_{44}), natural zeolite (A_{45}), oxic sediments (A_{46}), oxidized bituminous coal (A_{47}), peanut hull carbon (A_{48}), phosphorylated wood (A_{49}), poly (EG-DMA-HEMA) microbeads (A_{50}), potanogeton luscers biomass (A_{51}), polyacrylamide grafted tin (IV) oxide gel (A_{52}), purolite C 160 (A_{53}), raw charcoal (A_{54}), rice husk ash (A_{55}), rice paddy soil (A_{56}), rizopus arrhizus (a filamentous fungus) (A_{57}), saw dust (A_{58}), sepiolite (A_{59}), soils (A_{60}), sphagnum moss peat (A_{61}), titanium dioxide (A_{62}), unicellular green algae (A_{63}), waste lignite coal (A_{64}), waste biomass (A_{65}), waste Fe(III)/Cr(III) hydroxide (A_{66}) and pyrolucite (A_{67}).

Dr Ali Mohammad is Reader in the Department of Applied Chemistry, Z H College of Engineering and Technology, Aligarh Muslim University, Aligarh. He received his MSc degree in 1972, MPhil in 1975, PhD in 1978 in Chemistry with specialization in Analytical Chemistry and DSc in 1996, in Applied Chemistry, from Aligarh Muslim University, Aligarh, India. He is the author or co-author of 80 research papers and two book chapters. He has edited or reviewed over 160 scientific journal articles. His research interests are in the areas of Solid State Chemistry, Trace Analysis, Chromatography and Environmental Analysis. He is a member of several scientific and chemical societies. He is also serving as an editor of Journal of Chemical and Environmental Research and is a life member of Indian Association for History and Philosophy of Science

Mr Mohamed Najar P A is currently working as a research scholar in the Department of Applied Chemistry, Z H College of Engineering and Technology, Aligarh Muslim University. He obtained his MSc degree in 1992 in Chemistry and MPhil in 1994 in Applied Chemistry and has a throughout first class career. His research work is mainly concerned with Thin-Layer Chromatographic Studies of Transition Metals and Rare Earth Chlorosulphates. He has published a few papers in Indian and foreign journals of high repute and co-authored reviews on TLC analysis of Pesticides and Treatment Methods for Heavy Metal Pollutants with Dr Ali Mohammad. Presently, he is working in the Rubber Research Institute, Kottayam, Kerala, as an Analytical Trainee. He has almost completed his doctoral work and will be awarded degree by 1997 end.

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96)

Metals	Adsorbent	Comments/remarks	Ref.
Cd	A_{22}	Sorption capacity increases with the desorption of organic matter	21
Cd, Pb, Sr	A_{26}	Maximum removal was achieved. Adsorption of Cd and Pb is more by undried tea than dried tea	22
Cr (III)	A_{20}	Adsorption on pure MnO_2 or Fe_2O_3 was dependent upon pH. Very low adorption occurred below pH 3 and 8.5, respectively. Adsorption of Cr (VI) was less than Cr (III) and was affected by ionized Fe_2O_3 and organic matter conetnt in soil	23
Cd, Zn	A_{55}	Addition of zinc affects the cadmium adsorption	24
Cu	A_{60}	Various soils were tested, but maximum adsorption occurredin rhizosphere soils	25
Pb	A_{45}	The adsorption properties of the metal were studied	26
Hg	A_2	Complete removal of Hg achieved	27
Zn	A_{12}	Based on thermodynamic calulations, experimental results.and earlier published work, a model of Zn interaction in soil was proposed. According to the model, adsorption of the metal on Fe_2O_3 is initial and fast reaction, followed by slower diffusion of Zn into the hydrated layer of Fe_2O_3. $ZnFeO_4$ was the most probable solid phase which could formed in soils	28
Zn	A_{12}	adsorption of Zn is maximum at pH 298.0. Clay particles (< 0.01 mm diam) and $CaCO_3$ content also enhance Zn adsorption in soil	29
Heavy	A_{49}	Powders of todomatsu (*Abies sachaliensis* Master), Karamtsu (*Larix leptolepis* Gordon), Shinanoki (*Tilia japonica Simonkai*) shirakanba, (*Betula playphyllover, japonica Hure*) and concentrated cellulose phosphylated with a matrix	30

—Contd

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96)   — (Contd)

Metals	Adsorbent	Comments/remarks	Ref.
		of dimethylamide, H_3PO_4 and urea. Adsorption of heavy metal ions on phosphorylated wood powders was examined. Adsorption by treated adsorbent was 50-times and 20-times more than treated powders	
Cr(IV)	A_{20}, A_{60}	80 percent removal at optimum pH (2.0) at a Cr(VI)/L ratio > 0.00416. The adsorption capacities calculated by Freundlinch Adsorption Isotherm, gave 5.61 and 3.54 mg/g of Cr (IV) removal at pH 2.0 for distilled and tap water, respectively	31
Pb	A_2	Maximum removal was achieved but a little interference was made by Cr and Hg. The effect of surface area, and particle size of the adsorbent and pH on adsorption of the metal was studied	32
Metals	A_2	Efficient removal of metals from dilute aqueous solutions was observed from water and wastewater (A review with 13 references on metal removal from water and wastewater)	33
Cu, Pb	A_{10}	The method is convenient for preconcentrating the metals from a large aqueous phase and can be used to recover these metals from effluents of electroplating industries. Maximum removal of Cu : 99.8 percent and Pb 92.3 percent was achieved	34
Cr (VI)	A_{23}	Effective removal of the metal was achieved in equilibration time of 70 min and at a lower pH (i.e. 1). Adsorption obeys Ist order rate equation and Webber and Morris equation for pore diffusion	35
Cu, Zn, Cd	A_{20}, A_{60}	Adsorption in clays measured at pH 6.5 for Zn and Cd decreasesin the order vermiculite >montmorillonite > bentonite > illite > kaolinite. Copper shows relatively high affinity for kaolinite and illite. Organic matter content and free iron	36

                                                                              — Contd

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96) —(Contd)

Metals	Adsorbent	Comments/remarks	Ref.
		oxides were particularly important in detecting Cu and Cd adsorption, whereas for Zn, clay made a comparatively more important contribution. Maximum removal of the metals was achieved from aqueous solution. The process is pH dependent	
Cd	A_{46}	The surface charge of sediment particles was investigated by potentiometric titration with acid and base to understand the strong pH dependency of metal adsorption. Maximum removal occurred at pH 4.5 - 7.0	37
Co	A_{36}	Asorption of the metal is affected by Ca and Mg. Moreover the presence of synthetic organic chelating agents stronly inhibited the sorption of Co	38
Cd, Cu, Pb	A_1	Adsorption of cadmium was reduced by the presence of either pb or Cu. However, adsorption of pb and Cu was suppressed by Cd	39
Cr	A_2, A_{29}, A_{64}	Removal and recovery of Cr was achieved from chrome liquor from tannary industry. Chromium removal efficiencies of Cr precipitating agents like lime and washing soda were compared with that of the adsorbents	40
Cu	A_{25}	Adsorption of Cu was performed at various pHs The maximum efficiency of adsorption occurs when the sum of the fractions of species $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_2^{3+}$ in the solution reaches its maximum. With varied solutions, pH, the distribution of copper species is the detecting factor for maximum adsorption.	41
Ni, Cu, Zn, Cd	A_6	Adsorption of heavy metals was in the order Cu > Zn > Ni > Cd.	42

—Contd

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for
minimization of heavy metal content (1991-96)   — (Contd)

Metals	Adsorbent	Comments/remarks	Ref.
Ni, Cu, Zn, Cd	A_{21}	Highly selective for pb and Hg. Order of selectivity is pb> Hg> Ni> Cu> Zn> Cd. Enhancement of Hg, pb, Zn, Cu, Ni, and Cd sorption from aqueous solution by bituminous coal through impregnation was explored on using the batch adsorption process and down flow column studies	43
Cd	A_{18}	Maximum uptake of Cd (86.6%) occurred at pH 9.5. Lower surface loading favours uptake and an increase in surface loading from 0.5×10^{-4} to 2×10^{-5} M resulted in a decrease of removal efficiency from 80.3 to 41.0 percent	44
Ni, Pb	A_{11}	The tested material showed an adsorption capacity comparable to activated carbon	45
Cr (VI)	A_{62}	Sorption of chromium radionuclide was studied in the pH range 1 to 10 from aqueous solutions. The adsorption isotherm obtained was of the Freundlich type	46
Cr (VI)	A_{55}	Maximum removal was achieved at pH 2, with an equilibrium time of 4 h. The effect of pH, adsorbent, and solute concentration on the extent of Cr removal are reported	47
Co	A_{45}	The static and dynamic equilibrium adsorption of the metal by zeolite, the influence of pH, quality and quantity of interfering ions on adsorbate/ adsorbent systems were investigated. The influence of flow rate, activation and initial concentration on the sample of the break through curve was examined in dynamic regions. Maximum metal removal was achieved from aqueous solutions	48
Cu, Ni	A_{33}	A permanent reduction of Cu and Ni concentration to levels <0.1 mg/L was achieved from pre-cleaned waters	49

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96) — (Contd)

Metals	Adsorbent	Comments/remarks	Ref.
Cu	A_{57}	The adsorption data fitted the linear form of Langmuir adsorption equation. Maximum removal was achieved at 30-50°C	50
Pb,Ni,Cd, Cu,Zn	A_9	Proved to be a good adsorbent for the removal of all toxic metals	51
Zn	A_{18}	Adsorption of the metal ion on montmorillonite, kaolinite and bentonite was investigated by spectrophotometry and radiometry. The adsorption isothermsfit a Freundlich type equation. A markedeffect of Mg (II) and Zn (II) adsorption was observed in the case of bentonite. The process depends on the pH of each clay suspension	52
Cu	A_{43}	$ZnCl_2$ activated carbon and steam activated carbon prepared from rice husk were used for this study. The surface area of these carbons was detected by N adsorption at 196°C. Treatment with HNO_3 creates acidic contents on the carbon surface. Effluent removal was achieved from aqueous solution	53
Pb	A_{60}	Greater amount of the metal was adsorbed by soils with higher silt clay as compared to sandy soils. No significant difference in isotherm parameters was observed with EDTA concentration of 0.01 - 0.10 M, significantly altering adsorption/ desorption of Pb in soil	54
Cr	A_4	The adsorbents tested for the 55removal of metal ions from tannary waste include zeolite 3A, 5A and 13 X, the hydroxide form of Amberlite IR 120, ion - exchanger resin. The metal adsorption on to Amberlite IR 120 was evaluated in terms of pH, stability of the resin,Cr concentration and selectivity of the resin towards Cr in the presence of competing ions such as Na. The resin was stable at pH 1-11 and equilibriumtime of 20 min gave maximum adsorption.	55

— Contd

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96) —(Contd)

Metals	Adsorbent	Comments/remarks	Ref.
Pb,Th,Pu	A_{30}	Maximum removal is achieved from aqueous solutions. Adsorption decreases with increasing carbonate alkalinity	56
Cu, Pb	-	Sorption and desorption of the metals on river sediments in the presence of synthetic complexing agents. The results showed that sorption of Cu is strongly hindered by EDTA and NTA and this effect occurs with increase of the amount of complexing agent. At the beginning of the desorption process, the increase of released metal ions is found to be more initially	57
Pb	A_9	The applicability of blast furnace sludge as an adsorbent to remove heavy ketals from industrial effluents was evaluated. Adsorption data, fit the Langmuir equation well. The adsorption capacity is <80 mg pb/g	58
Co	A_{16}	Metal removal from dilute aqueous solution was achieved	59
Zn, Cd	-	Sorption of Zn and Cd on hydroxyapatite surfaces	60
Cr,(VI)	A_{26}	Maximum removal is achieved from mixed solution. Effect of concentration, time, pH and temperature of mixed solution were investigated. The adsorbate percentage of Cr (VI) on used tea is only slightly lower than on fresh tea	61
Heavy Metals	-	Heavy metals are precipitated from aqueous solution of electrolytes by an action of high voltage pulses current on aqueous solution. A crystal-like film was formed on the electrolyte surface. A mechanism involving the charge accumulation of microbubbles is proposed	62
Mo, Co, Ni, Zn	A_{34}	Maximum removal is obtained from different electrolyte solutionsby amorphous $Fe(OH)_2$.	63

— Contd.

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96)   —(Contd)

Metals	Adsorbent	Comments/remarks	Ref.
		Adsorption , iso-therm at constant pH indicates that adsorption of these trace metals is non-Langmuirian at the concentrations studied. Co and Ni exhibit strong competition for higher energy surface sites. Mn shows little and Zn exhibits no competition for surface sites. Adsorption of Zn is therefore almost independent of the nature of the background electrolyt solution	
Cr (VI)	A_7	Adsorption of low level Cr (VI) from aqueous solutions. Radio tracer technique was used for the study of adsorption of Cr (VI) traces on Bi-trioxide from aqueous solution. Chemical reactions between sorbent and sorbate have been established by IR studies. Effect of pH (2-10), concentration ofchromate solution (10^{-6} -10^{-2} M) and temperature (303-323°K) and interfering foreign ions was investigated	64
Pb	A_{34}	Removal efficiency of the metal is high with increasing pH, temperature and Pb concentration. Shaking time, pH, temperature and metal ion concentration are the depending parameters. The results are analysed in terms of the Langmuir isotherm over the entire range of matal concentration. In addition to two possible adsorption mechanisms, ion exchange and $Pb(OH)_2$ precipitation, a chemical reaction is indicated by the increase of heat of adsorption	65
Pb	A_{32}	Ammonia treated peat was used to remove pb from waste waters. Initial Pb concentrations of 100-200 mg/l were decreased to < 1 mg/l at sorption capacity 230-280 g equiv/m³. Final pb concentration < 0.01 mg/l are obtained at 60-80 g equiv /m³	66
Cd	A_{66}	Desorption of Cd was 70 percent at pH 3.80. The equilibrium data could be described well by Langmuir and Freundlich isotherm equations. Effect of initial metal ion concentration, agitation time, temperature and pH were investigated by	67

— Contd

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96) — (Contd)

Metals	Adsorbent	Comments/remarks	Ref.
		waste Fe (III) hydroxide. The intra-particle diffusion of Cd (II) through pores in the adsorbent was shown to be the main rate limiting step	
Cr (VI)	A_{58}	Maximum adsorption capacity was 4.44 mg/g. Analysis of the equilibrium isotherm data was undertaken using the Freundlich and Langmuir isotherms	68
Cu, Ni	A_{57}	Sorption phenomena was expressed by the Freundlich adsorption isotherm.	69
Cu, Pb, Cr(VI)	A_{14}	Adsorption of Cu, pb and Cr (VI) in wastewaters by the adsorbent was studied as a function of flow rate and inlet adsorbent was studied as a function of flow rate and inlet metal ion concentration in packed bed column reactors. The highest metal uptake efficiencies were obtained by immobilized *C.vulgaris* and *Z. ranigera* in the adsorption of Cu^{2+}/ Pb^{2+}	70
Zn	A_{29}	Adsorption of Zn was studied in glass columns and in clarifier model. Clarifier performed better in COD removal and in the adsorption of zinc	71
Cd	A_{35}	Removal of cadmium was investigated by the sorbent at an ultrafine particle size range. Typical adsorption isotherms of Langmuir type were calculated, zeta-potential measurement of other hydroxy apatite and calculated zeta-potential measurements of the hydroxyapatite particles and the release of Ca were also examined and related to possible mechanism occurring during the Cd removal. The influence of main sorption parameters was examined	72
Co,Pb,Cr	A_{30}	Adsorption was carried out in the pH range of 4.0-10.0. The metal ion adsorption is strongly pH dependent and the adsorption capacity is in the	73

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96) —(Contd)

Metals	Adsorbent	Comments/remarks	Ref.
		order Cr>pb> Cd. The highest adsorption medium observed was the $1 \times 10^{-3}M$ KNO_3. The surface titration data showed that the isoelectric point of geothite was 7.2	
Cu	A_{54}	Adsorption of copper was studied at 293°K. A method for preparing raw charcoal was established and the main adsorption characteristics of metal ions as well as the static and dynamic conditions of the adsorption process were examined. The presence of other metal ions in the solution decreases the adsorption capacity	74
Cu, Zn	A_3, A_{59}	Effect of pH, time, contact time and adsorbent concentration on heavy metal uptake were investigated. The experimental data were interpreted in the form of Freundlich and Langmuir type isotherms. Adsorption capacity of a natural zeolite was compared with the two commercial adsorbents	75
Heavy metals	A_{42}	Removal efficiency on a molar basis of the series of metals studied has been detected to be as follows :cu (II) > Pb(II) Zn(II) > Cd(II). Textural data indicate that the nature of the available surface area has an important role in determining the capacity of the adsorbent	76
Cr (VI)	A_8	Removal efficiency of Cr(VI) from wastewaters of steel plants was > 95 percent. The adsorption process followed first order kinetics with respect to metal ion concentration	77
Cr (VI)	A_{61}	Adsorption of Cr(VI) was pH dependent. The exhausted peat can be regenerated with 1M NaoH. The capacities of Irish peat are greater than Chinese peat	78

— Contd

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96) — (Contd)

Metals	Adsorbent	Comments/remarks	Ref.
Cu, Cd, Mn(III)	A_{47}	Potential applications for treating effluents, especially those containing oxidizing ions are discussed. Effective removal of Cu, Cd and Mn from aqueous solution along with possible flow sheet options, the effect of oxidation, treatment, metal ion concentration and solution pH on metal uptake kinetic was studied	79
Cu	A_{51}	Maximum copper removal was at pH 5.0-6.6 When Cu was present in the Cu(II) form. Sorption followed Langmuir isotherm with saturation at 35 mg/g. Main mechanism for heavy metal uptake was ion-exchange	80
Pb	A_9	Residence time and temperature coefficient on sludge adsorption efficiency was studied for the particular case of Pb(II). Adsorption data fit the Langmuir equation well. Adsorption capacity was < 80 mg Pb/g	81
As (V)	A_{19}	The adsorption potential of chrome sludge, a waste material from electroplating industry was investigated. The parameters studied included sorbent dosage. The process was rapid and followed Langmuir isotherm. Maximum adsorption capacity of As(V) from aqueous solution was 21 mg/g	82
Cr (III)	A_5	Affinity of metal sorption was in Ni,Cu,Zn the order Pb(II) > Cu(II) Ni(II) > PbCr(III) > Zn(II), and was temperature, initial concentration and pH dependent. The equilibrium data followed Langmuir type isotherm with maximum capacities 8.55 and 13.46 mg/g of Cu in electroplating waste and synthetic solution, respectively. pH 4.5 being optimum value	83
Pb	A_{48}	Quantitative removal of 20 mg Pb(II)/l by 0.3 g carbon per litre aqueous solution was observed in the pH range of 3.0-10.0, over a range of initial	84

Table-1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96) —(Contd)

Metals	Adsorbent	Comments/remarks	Ref.
		metal ion concentration 10-20 mg/l (agitation time 5-100 min). The adsorption of Pb (II) obeyed Langmuir isotherm	
Cu	-	Adsorption obeyed Langmuir adsorption isotherm. The suitability of the adsorbent for treating copper plating industry wastewater was tested	85
Pb	A_{39}	Separation and removal of Pb ion from aqueuous solutions with chelating ion exchange resin having phosphate group. Adsoption of Pb ion to the resin solution and its recovery with mineral acid etc. are described. Repeated use of the resin for Pb ion adsorption after washing with H_2O possible.	86
Ni, Cu	-	Chitosand and Ca-alginate were separately prepared from crab chitin and algin in pellet form for adsorption of Cu and Ni	87
Ni	A_{24}	The performance of coconut fibre compost as an effective adsorbent for the removal of Ni is discussed. The effect of operational pH, compost dose and particle size of adsorbent is examined	88
Heavy	-	Removal of heavy metals after uptake Metalsby the microorganism and of organic substances by biological decomposition as well as by adsorption is discussed	89
Cr (VI)	A_{28}	Batch conversion studies show that the adsorbent can be used to remove the metal from aqueous solutions. The process is pH dependent and a pH of 1.0 gives best result	90
Cu	-	Optimum pH for maximum adsorption is 2-5. The carboxyl groups play a significant role in the adsorption mechanism	91
Cu,Cd, Zn	A_{15}	Adsorption of Zn and Cd is higher than that of Cu. the effect of pH is insignificant. The metal	92

— Contd

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96) —(Contd)

Metals	Adsorbent	Comments/remarks	Ref.
		adsorption capacity of the adsorbent decreased with its phytic acid content reduction	
Cr	A_{15}	The adsorption of Cr(III) is increased with the increase in temperature between 4 and 50°C. pH betweeen 5 and 7 did not have much effect on the adsorption. Langmuir and Freundlich isotherm models fit the equilibrium data for Cr(III)	93
Cu	A_{27}	Langmuir and Freundlich isotherm operations were tested to describe. Cu^{2+} adsorption on to the composite adsorbent	94
Pb	A_{52}	Effect of contact time, initial concentration, pH, and temperature were examined. The adsorption follows first order kinetics with maximum uptake at pH 5.5. Spent adsorbent can be regenerated by acid treatment and reused	95
Cu, Cd, Zn, Pb	A_{50}	The adsorption rate and capacity of the microbeads for the metalions were investigated at different pH values (1.5-7.5). Repeated use of the adsorbent is possible	96
Co,Ni,Cu, Pb,Fe	-	Experimental conditions for 100 percent removal were optimised	97
Cd	A_{63}	Bioremoval capabilities of micro algae (*Chlorella pyrenoidosa* and *Chlamydomonas reinhardtii*)have been studied	98
Zn, Cd	-	The metal removal increases with the increase in temperature but decreases on increasing the molar metal/carbon ratio	99
Cu,Pb,Cr, Ni,Co	A_{17}	Accumulation and recovery of copper from mining wastewater were investigated	100
Zn	A_{65}	The influence of pH, temperature, biomass concentration time and initial Zn concentration on	101

—Contd

Table 1 : Adsorption treatment of water and wastewater using different adsorbents for minimization of heavy metal content (1991-96)   —(Contd)

Metals	Adsorbent	Comments/remarks	Ref.
		adsorption of Zn from dilute $ZnSO_4$ solution by activated sludge was described	
Pb	A_{61}	The studies include the effect of pH and temperature on kinetics of adsorption. Adsorption data followed Langmuir models	102
Cu, Ni	A_{61}	Examination of adsorption of Cu and Ni form mono and bi-solute systems. Pore diffusion is the rate controlling step and the presence of Cu ions reduces the Ni. Kinetics of adsorption is best described by a second - order expression	103
Pb,Zn,Cd	A_{67}	Adsorption of metal ions follow the order $Pb^{2+} > Zn^{2+} > Cd^{2+}$ with maximum adsorption of Pb^{2+} (100%) around pH 7. The kinetic data follow the Freundlich adosorption isotherm	104

Note : The metal ions are in their usual valency state othervise specified.

References

1   Thom I, Walting H & Daryacot A, *Sci Total Environ*, **4** (1975) 325.

2   *Battelle Columpus Laboratories, US EPA Report 12010 EIE 11/71*, 1971.

3   Vishwakarma P P, Yadava K P & Singh V N, *Pertanika*, **12** (1989) 3.

4   Gosset T, Trancart J L & Thevenot D R, *Wat Res*, **20** (1986) 1.

5   Guthrie R E & Lourle S H, *Aust J Chem*, **21** (1968) pp 2437-2443.

6   Kulkami M V & Rane V C, *Chem Age India*, **31** (1980) pp 499-503.

7   Ajmal M, Nomani A A & Ahmad A, *Wat Air Soil Pollut*, **23** (1984) pp 119-127.

8   Gupta S K & Chen K Y, *J Wats Pollut Cont Fed*, **50** (1978) pp 493- 505.

9   Salim R, *Wat Res*, **17** (1983) pp 423-429.

10   Lee S E, Shin H S & Paik B C, *Wat Res*, **23** (1) (1989) pp 67-72 .

11   Kumar P & Dara S S, *J Polym Sci*, **19** (1981) pp 397-402.

12   Okiemen F E, Ogbeitun D E, Nwala G N & Kunsah C A, *Bull Environ Contam Toxic*, **34** (1985) pp 860-870.

13   Randall J M, Berman R L, Carrat V & Waiss A C (Jr), *Forest Prod J*, **24** (1974) pp 80-84.

14   Kumar P & Dara S S, *Indian J Environ Health*, **22** (1980) pp 196- 202. .

15   Larsen V J & Schierup H, *J Environ Qual*, **10** (1991) pp 188-198.

16   Cullen G V & Siviour N G, *Wat Res*, **16** (1976) pp 1357-1366.

17   Coupel B & Lalancette J M, *Wat Res*, **10** (1976) pp 1071-1076

18   Srivastava S K, Tyagi R & Pant N, *Wat Res*, **9** (1989) pp 1161-1165.

19   Rowley A G, Husband F M & Cunninghan A B, *Wat Res*, **18** (1984) pp 1981-1984.

20   Singh D K, Tiwari D P & Saksena D W, *Wat Res*, **35** (1993) pp 169- 177.

21   Low K S & Lee C K, *Pertanika*, **14** (1) (1991) pp 83-86.

22   Zhao F & Gao S, *Lizi Jiaohaun Yu Xifu*, **7** (3) (1991) pp 211-213.

23   Wu D & Lu W, *Shanghai Huanjing Kexue*, **10** (2) (1991) pp 19-23.

24   Wu D & Lu G, *Shanghai Huanjing Kexue*, **10** (8) (1991) pp 20-23.

25   Wang J & Liu Z, *Huanjing Kexue Xuebao*, **11** (2) (1991) pp 178-186.

26   Minamisawa H, Yamanaka H, Arai N & Okutani T, *Nippon Kagaku Kaishi*, **12** (1991) pp 1605-1611.

27   Wang L C, Yang B & Liu D, *Huaxue Gongching*, **19** (2) ; **52** (1991) pp 53-57.

28   Sadiq M, *Wat Air Soil Pollut*, **57 & 58** (1991) pp 411-421.

29   Wu J, Gao X, Gao B, Yang G, Lu L & Guan L, *Turang Xeubao*, **28** (4), (1991) pp 452-456.

30   Saito N & Aoyama M K, *Rinsan Shikenjoho (Hokkaido)*, **5** (6) (1991) pp 15-18.

31   Periaswamy K, Srinivasan K & Murugan P K, *Indian J Environ Health*, **33** (4) (1991) pp 433-439.

32   Gajhate D G & Saxena E R, *Indian J Environ Health*, **33** (3) (1991) pp 374-379.

33   Pitter P, *Sb Vys Sk, Chem-Technol Praze F Technol Vody Prostredi F*,(1991) pp 77-102; *Chem Abstr*, **117** (1992) 177800 W.

34   Kaur A, Malik A K, Verma N & Rao A L J, *Indian J Environ Prot*, **11** (6) (1991) pp 433-435.

35   Roa S S P, Mise S R & Manjunatha G S, *J Environ Sci Health Part- A*, **A-27** (8) (1991) pp 2227-2241.

36   Halen H, Van B R & Cloos P, *Pedologie*, **41** (1) (1991) pp 47-88.

37   Fu G & Allen H E, *Wat Res*, **26** (2) (1992) pp 225-233.

38   Bangash M A, Hanif J & Khan M A, *Waste Manage (NY)*, **12** (1) (1992) pp 29-38.

39   Chen C, Lee D Y & Houng K H, *Zhongguo Nongye Huaxue Huizhi*, **30** (1) (1992) pp 83-99.

40   Kannan N Y & Vijayraghavan A, *Indian J Environ Protect*, **12** (1) (1992) pp 46-49.

41   Luo C S & Huang S D, *J Chim Chem Soc* (Taipei), **39** (3) (1992) pp 223-230.

42   Jia J, *Miner Met Environ*, (*Pap Int Conf*), (Elsevier, London UK), 1992, pp 402-406.

43   Singh D K & Lal J, *Pollut Res*, **11** (1) (1992) pp 37-42.

44   Sharma Y C, Rupainwar D C, Upadhyay S N & Prasad G, *Chem Environ Res*, **1** (1) (1992) pp 95-101.

45   Donati A, Seitz M, Morselli L, Zappoli S & Gheduzzi A, *Toxicol Environ Chem*, **35** (1-2) (1992) pp 87-92 .

46   Bhutani M M, Kumari R & Mitra A K, *J Radioanal Nucl Chem*, **159** (2) (1992) pp 343-351.

47   Bansal T K & Sharma H R, *Indian J Environ Protect*,. **12** (3) (1992) pp 198-201.

48   Chielewska-Horvathova E & Lesney J, *J Radioanal Nucl Chem* **166** (1) (1992) pp 41-53.

49   Leimann H, *WLB Wasser Luft Boden*, **36** (5) (1992) pp 52-54.

50   Begum S, *Sci Int (Lahore)*, **4** (1) (1992) pp 67-68.

51   Jallan G & Panday G S, *Res India*, **37** (3) (1992) pp 143-145.

52   Fujiyoshi R, Eugene Andriamisamanana S & Katayama M, *Appl Radiat Isot*, **43** (10) (1992) pp 1223-1226.

53   Youssef A M & Mostafa M R, *Indian J Technol*, **30** (8) (1992) pp 413-416.

54   Peters R W & Shem L, *Environ Prog*, **11** (3) (1992) pp 234-240.

55 O'Dwyer T F & Hodnett B K, *Key Eng Mater*, **72-74** *(Mater Adv Technol Appl)*, *(1992) pp 529-534.*

56 Murray J W & Coughlin B R, *Water-Rock Interact Proc Int Symp*, **7** (1) (1992) pp 55-57.

57 Runkel M & Stork G, *Vom Wasser*, **81** (1991) pp 387-396.

58 Singh S P & Nayyar V K, *J Indian Soc Soil Sci*, **41** (2) (1993) pp 270-273.

59 Shakir K, Benjamin K & Aziz M, *J Radioanal Nucl Chem*, **173** (1) (1993) pp 141-152.

60 Xu Y, Schwartz F W & Traina S, *J Environ Sci Technol*, **28** (8) (1994) pp 1472-1480.

61 Yang C, Yang Z & Mu G, *Huanjing Huaxue*, **13** (2) (1994) pp 176-180.

62 Malinin A N, Sabinin V E & Sidoro A N, *Pisma Zh. Tekh Fix*, **20** (1) (1994) pp 57-61.

63 Kanungo S B, *J Colloid Interf Sci*, **162** (1) (1994) pp 93-102.

64 Bhutani M M & Kumar R, *J Radioanal Nucl Chem*, **180** (1) (1994) pp 145-153.

65 El-Shahat M F, Abdel-Hakim M, Burham N & El-Nagger I M, *Mater Sci*, **18** (2-4) (1994) pp 23-30.

66 Milchenko D V, Yuffa A, Ya & Kubasova E B, *Zh Ekol Khim*, **1** (1994) pp 78-83.

67 Chand S, Agarwal V K & Kumar P, *Indian J Environ Health*, **36** (3) (1994) pp 151-158.

68 Zaraas M A, *Adsorpt Sci Technol*, **12** (2) (1995) pp 129-138.

69 Sag Y & Kutsal T, *Chem Eng J (Lausanne)*, **58** (3), (1995) pp 265- 273.

70 Sag M Nourbakhshs M, Aksu Z & Kutsal T, *Turk J Eng Environ Sci*, **19** (2) (1995) pp 145-157.

71 Gaikwad R W & Bhardwaj V, *Indian J Environ Health*, **37** (2) (1995) pp 111-114.

72 Mandjiny S, Zouboulis A T & Matis K A, *Sep Sci Technol* **30** (15) (1995) pp 2963-2978.

73 Jinadasa K B P N, Dissanayake C B & Weerasooriya S V R, *Int J Environ Stud*, **48** (1) (1995) pp 7-16.

74 Khalfaoui B, Meniai A H & Borja R, *J Chem Technol Biotechnol*, **64** (2) (1995) pp 153-156.

75 Mirada F, Garica J, Leyenda O, & Lodaraes C, *First ChemE Res Event-Eur, Conf Yong Chem*, **1** (1995) pp 185-187.

76. Allen S J & Choudhury M A, *First ChemE Res Event-Eur, Conf. Young Res Chem Eng*, **1** (1995) pp 375-377.

77 Patnaik L N & Das C P, *Indian J Environ Health*, **37** (1) (1995) pp 19-25.

78 Sharma D C & Forstes C F, *Process Biochem, (oxford)*, **30** (4) (1995) pp 293-298.

79 Bodine Donna L & Doyle Fiona M, Treatment Minimization Heavy Metals As containing Wastes, *Proc Int Symp*, (1995) pp 81-93.

80 Schneider I A H, Desouza M L & Rubio J, *Sep Process Proc Symp*, (1995) pp 49-60.

81 Lopez Felix A., Perez Carlos, Sainz Enrique & Alonso Manuel, *J Chem Technol Biotechnol*, **62** (2) (1995) pp 200-206.

82 Low K S & Lee C K, *Environ Technol*, **16** (1) (1995) pp 65-71.

83 Low K S, Lee C K & Leo A C, *Bioresour Technol*, **51** (2 & 3) (1995) pp 227-231.

84 Periaswamy K & Namasivayam C, *Sep Sci Technol*, **30** (10) (1995) pp 2223-2237.

85 Periaswamy K & Namisivayam C, *Chemosphere*, **32**, (1996) pp 769-781.

86 Egawa H, *Jpn Kokai Tokkyo Koho JP 08 10, 763* [96-763] (ClBOIJ 20/10), 16 January 1996, App l. 94/173, 320, 01 July 1994, pp 6 (Japan); *Chem Abstr*, **124** (1996) 241112x.

87 Gujjaro L, John Wase D A & Forster C F, *Second I Chem· Eng Res Event Eur Conf Young Res Chem Eng*, (1996) pp 624-626.

88 Enders R & Jekel M, *Vom Wesser*, **86** (1996) pp 141-155.

89 Suzuki V, Mochidzuki K, Takenchi Y, Ya G Y, Fukudo T, Amakura H & Abe H, *Sep Technol*, **6** (2) (1996) pp 147-153.

90 Basinco S, Roussy J, Guibal E & Le C, *Environ Technol*, **17** (1) (1996) pp 55-62.

91 Gardea-Torresdey J L, Cano - Aguileral W, Tiemann K J & Gutierrez - Carona F, *J Hazard Mater*, **48** (1-3) (1996) pp 171-180.

92 Al-Asheh S & Duvnjak Z, *J Hazard Meter*, **48** (1-3) (1996) pp 83-93.

93 Al-Asheh S & Duvnjak Z, *Water Qual Res J Can*, **31** (2) (1996) pp 319-328.

94 Wang T & Anderson P R, *Proc Ind Wast Conf*, **50** (1996) pp 227-235.

95 Shubha K P & Anirudhan T S, *Indian J Chem Technol*, **3** (1) (1996) pp 55-57.

96 Denzil A, Salih B & Diskin E, *React Funct Polym*, **29** (1) (1996) pp 11-19.

97 Reichert J & Binner J G P, *J Mat Sci*, **31** (5) (1996) pp 1231-1241.

98 Khoshmanesh A, Lanson F & Prince I G, *Chem Eng J*, **62** (1) (1996) pp 81-88.

99 Marzel P, Seco A, Gabaldon C & Ferror J, *J Chem Technol Biotechnol*, **66** (3) (1996) pp 279-285.

100 Yanaoka Y, Takimura O, Fuse H, Kamimura K & Murakami K, *Nipp on Kagaku Keishi*, **6** (1996) pp 566-571.

101 Mishra S P & Chaudhury G R, *Int J Environ Stud*, **50** (2) (1996) pp 117-124.

102 Ho Y S, Wase D A J & Forster C F, *Water SA*, **22** (3) (1996) pp 219- 224.

103 Ho Y S, Wase D A J & Forster C F, *Environ Technol*, **17** (1) (1996) pp 71-77.

104 Ajmal M, Rao R A K & Siddiqui B A, *Environ Monit Asses*, **38** (1) (1995) pp 25-35.

Synthesis and Characterization of Amphoteric Ion Exchangers

Sushila Amin* and R N Kapadia

Department of Chemistry, M S University of Baroda, Baroda 390 002, India

Synthesis of furfural-benzidine-phenolic derivative type amphoteric resins using gel technique is reported. The monomers employed included gallic acid, p-hydroxy benzoic acid, salicylic acid and hydroquinone. Physicochemical properties such as the total capacity, moisture retention ability, density, void volume fraction, rate of exchange, pH titration behaviour, apparent pK_a, pK_b and isoelectric point values and oxidation resistance have been studied. The effect of equilibration at different temperatures on the capacity of the resin, and swelling behaviour in various solvents have also been investigated.

Introduction

A number of studies have been carried out earlier on the furfural type resins[1-3]. The synthetic complexing resins such as amphoteric ion-exchange resins, can find use in column and thin layer chromatography, ligand exchange chromatography, membrane formation, desalination, waste water management, etc.[4]. In continuation of our work on furfural type resins[5], we now report synthesis of the following new resins using Schiff base (furfural-benzidine) and gallic acid, p-hydroxy benzoic acid, salicylic acid and hydroquinone:

Furfural - benzidine - gallic acid (Fu-Ben-GA)
Furfural - benzidine - p-hydroxybenzoic acid (Fu-Ben-pHy)
Furfural - benzidine - salicylic acid (Fu-Ben-SA)
Furfural - benzidine - hydroquinone (Fu-Ben-Hy).

Experimental

Synthesis of Resin

Schiff base was synthesized using furfural and benzidine. Two moles of gallic acid, p-hydroxy benzoic acid, salicyclic acid or hydroquinone were dissolved in DMF in a 250 mL round bottom flask and 1 mole of Schiff base was added to it. The mixture was refluxed for 3h using p-TSA as the initiator. Gel formation occurred in about one hour and a hard mass

---

*Author for correspondence

was obtained, which was dark brown to black in colour depending upon the phenolic monomers used. The cured hard mass was then crushed to –60 to 100 BSS mesh size and washed with ethanol to remove unreacted monomers and low molecular weight products from the resins. The resins were dried at 100°C and stored in polyethylene bottles. All the resins were characterized by their physicochemical properties following the standard methods[6-11].

Estimation of the Rate of Ion Exchange

For the estimation of the rate of ion exchange at room temperature, 0.5g (–60 to 100 mesh) of resin was accurately weighted into each of the nine stoppered bottles and 100mL of 0.1N NaOH in 1N NaCl were added to each bottle and the resin was allowed to remain in contact for different periods of time, with intermittent shaking. At definite predetermined intervals, the solutions were decanted and an aliquot was titrated against a standard acid or alkali and from this the capacity at different time intervals was calculated.

Results and Discussion

The amphoteric ion exchange resins synthesized from Schiff base and various phenolic derivatives were insoluble in sodium hydroxide, hydrochloric acid and dioxane — the solvents in which the individual components are miscible or soluble. There-

fore, the resin appears to be a condensate product of phenolic derivatives with Schiff base.

The ion exchangers are fairly porous with average physical stability and good chemical resistance to acids and alkalis up to $3N$ strength. However, a change in colour was observed when converted from free acid/base form to its corresponding salt (Na or Cl) form or vice versa. The resins were obtained by polycondensation under mild reaction and curing conditions. The bond formation is possible through -C-C- bridge, as evident from IR spectra.

Table 1 — Elemental analysis

Resin	Theoretical, %			Experimental, %		
	C	H	N	C	H	N
Fu-Ben-GA	67.08	3.72	4.34	67.72	5.04	4.03
Fu-Ben-pHy	74.48	4.13	4.82	73.98	5.08	3.98
Fu-Ben-SA	74.48	4.13	4.82	73.79	5.35	4.46
Fu-Ben-Hy	73.38	4.31	5.03	73.09	5.16	5.23

Fu (Ben) GA

Fu (Ben) PHY
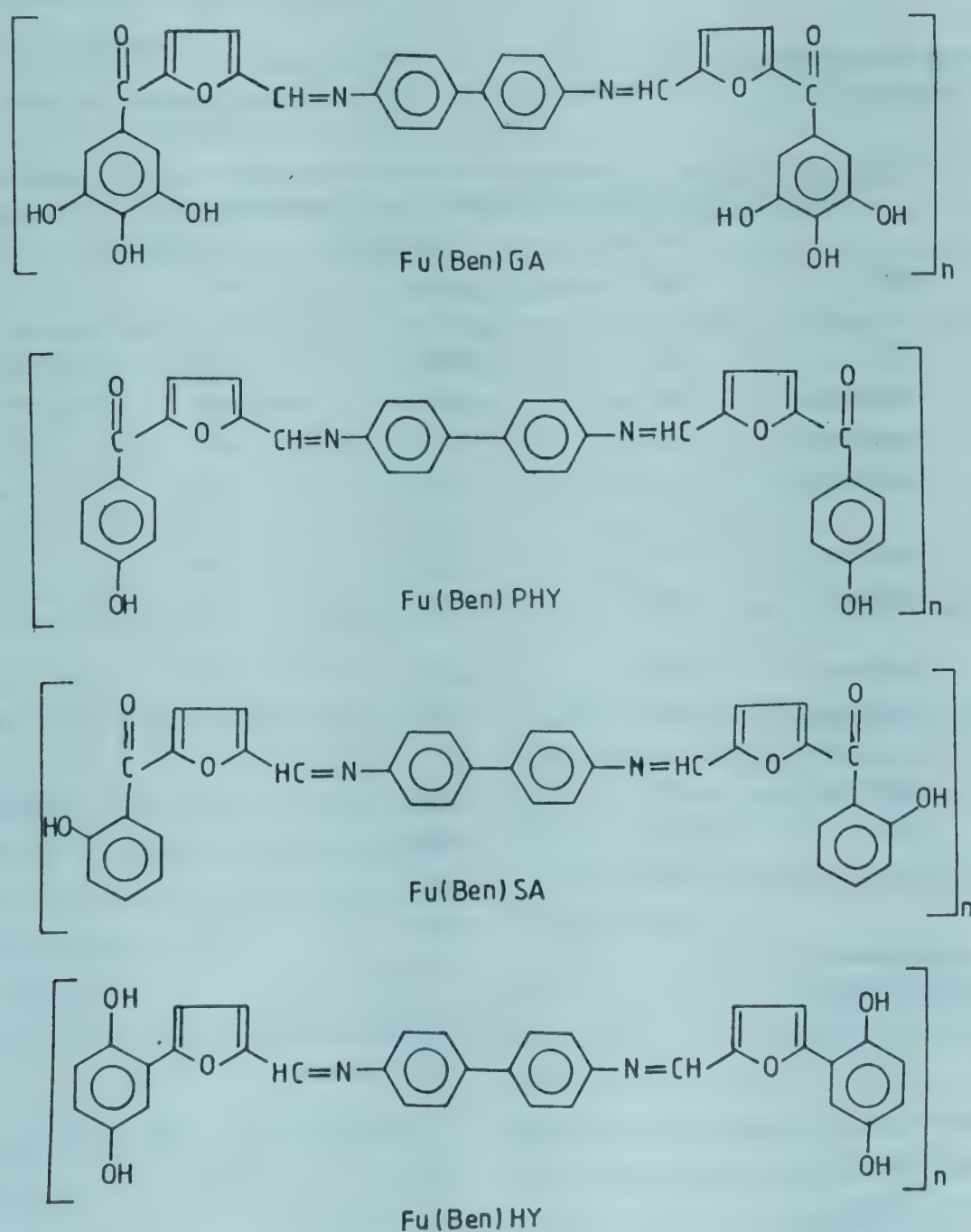
Fu (Ben) SA

Fu (Ben) HY

Chart 1
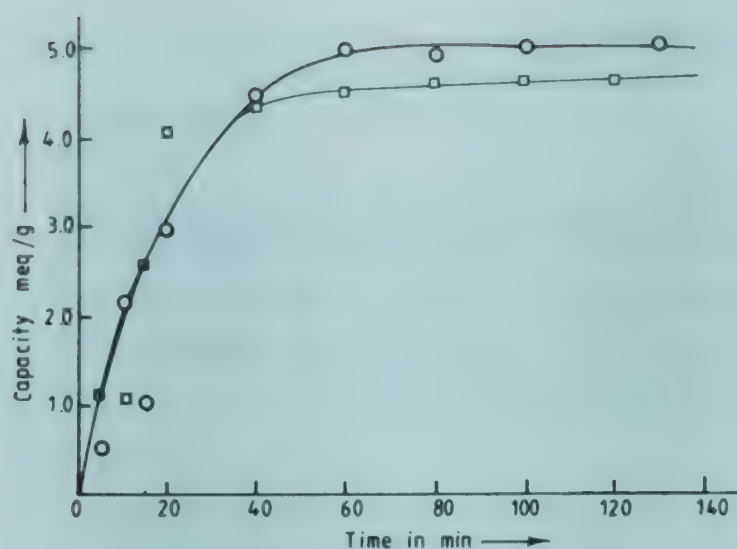
Fig.1 — Rate of exchange for cation
O — O Fu-Ben-GA; ▢ — ▢ Fu-Ben-pHy
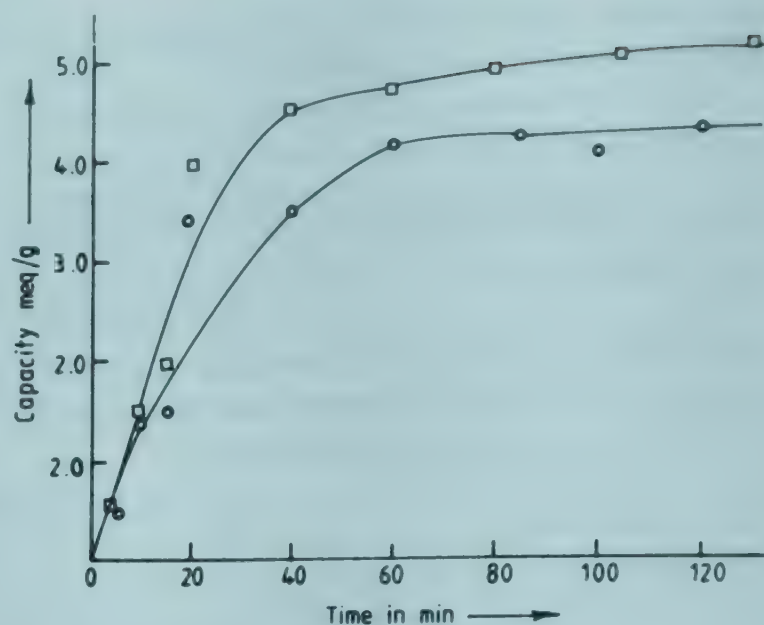
Fig.2 — Rate of exchange for cation
O — O Fu-Ben-SA; ▢ — ▢ Fu-Ben-Hy

Table 2 — Physicochemical characteristics of the ion-exchange resin

Property		Fu-Ben-GA	Fu-Ben-pHy	Fu-Ben-SA	Fu-Ben-Hy
Total capacity (Meq/g)	CEC*	5.45	4.65	4.13	5.01
	AEC*	5.99	5.51	5.38	5.41
Moisture, %	Acid form	5.22	4.9	4.01	5.01
	Base form	14.0	8.0	5.0	13.6
True density (dres g/cm^3)	Acid form	1.12	1.31	1.00	1.02
	Base form	1.10	1.23	1.01	1.28
Apparent density (dcol g/mL^3)	Acid form	0.29	0.32	0.28	0.24
	Base form	0.30	0.29	0.31	0.25
Void volume fraction	Acid form	0.74	0.75	0.72	0.76
	Base form	0.73	0.76	0.71	0.80
	pK_a	11.26	10.70	11.13	11.24
	pK_b	3.84	3.76	3.82	4.12
Isoionic point		7.55	7.23	7.48	7.68

*CEC =cation exchange capacity
*AEC =anion exchange capacity

Reversibility of ion exchangers has been established. On the basis of elemental analysis (Table 1), IR spectra, and physicochemical studies, we have postulated the structure of the resins as shown in Chart 1.

Moisture content (Table 2) of the resins was found to range from 4.02% to 5.22% for the acid form and 5.0% to 14.0% for the base form. The resins showed the following order of moisture content for cation and anion exchangers:
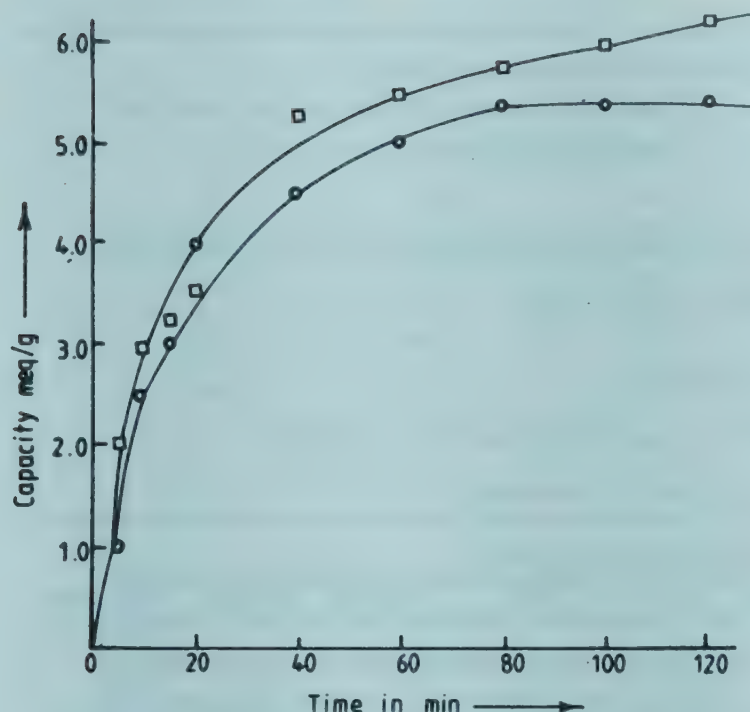
Fig.3 — Rate of exchange for anion
O — O Fu-Ben- GA; □ — □ Fu-Ben-pHy
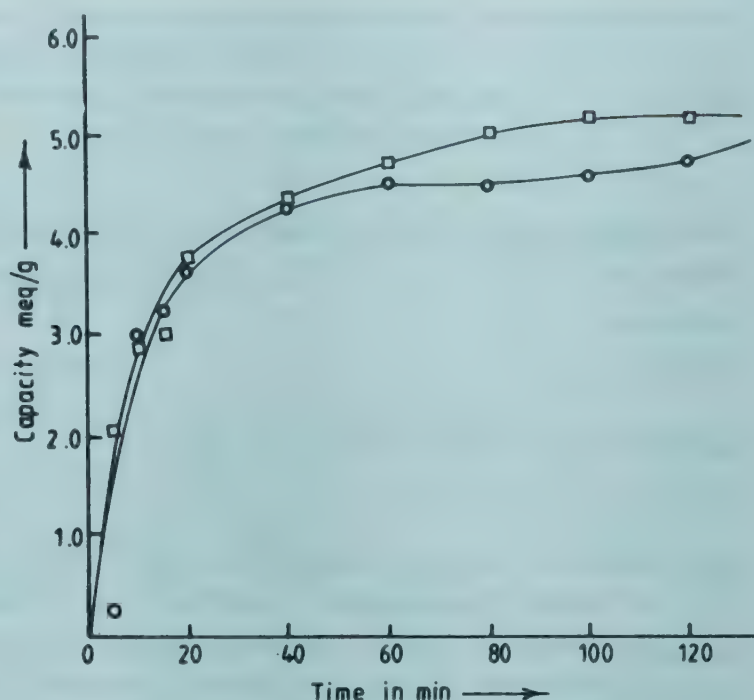
Fig.4 — Rate of exchange for anion
O — O Fu-Ben-SA; □ — □ Fu-Ben-Hy

Table 3 — Oxidation resistance of resin

Resin	Percentage moisture untreated exchanger		Percentage moisture H_2O_2 treated exchanger		Increase in content, %	
	Acid form	Base form	Acid form	Base form	Acid form	Base form
Fu-Ben-GA	5.22	6.26	14.03	16.93	8.81	10.97
Fu-Ben-pHy	4.90	5.15	12.48	15.43	7.58	10.28
Fu-Ben-SA	4.02	4.93	11.59	15.03	7.57	10.01
Fu-Ben-Hy	5.01	5.98	13.56	16.34	8.55	10.36

Fu-Ben-SA <Fu-Ben-pHy <Fu-Ben-Hy < Fu-Ben-GA.

The column density (Table 2) of these resins (acid and base forms) was low, suggesting little swelling percentage. All the resins (acid and base forms) had large void volume fraction (Table 2).

The rate of exchange for the resins as cation exchanger (Figs 1 and 2) as well as anion exchanger (Figs 3 and 4) was very high (diffusion controlled). In the case of resins as cation exchanger, it was observed that (i) 50% exchange occurred in 5 to 20 min, and (ii) the rate of exchange for these resins followed the order:

Fu-Ben-SA <Fu-Ben-pHy <Fu-Ben-GA < Fu-Ben-Hy.

In the case of resins as anion exchanger, it was observed that (i) 50% exchange occurred in 5 to 10 min, and (ii) the rate of exchange of these resins followed the order:

Fu-Ben-SA <Fu-Ben-Hy <Fu-Ben-pHy < Fu-Ben-GA.

The pK_a values for the resins are comparable to those of the compounds having phenolic hydroxy group (Table 2), indicating the weekly acidic nature of the matrix. The pK_b values are in the range of the base of medium strength. On oxidation, the resins acting as cation exchanger showed a higher increase in the percentage water content than those acting as anion exchanger (Table 3). The anionic form of these resins was less susceptible to oxidation than the cationic form. The anion exchange capacity of the

Table 4 — Effect of temperature of equilibration on the capacity of the resin

Resin	Total AEC (meq/g) of absolutely dry resins as determined at different temperatures, °C			Total CEC (meq/g) of absolutely dry resins as determined at different temperatures, °C		
	30°	50°	70°	30°	50°	70°
Fu-Ben-GA	5.21	5.22	5.31	5.34	5.31	5.29
Fu-Ben-pHy	5.13	5.14	5.23	4.62	4.34	4.23
Fu-Ben-SA	5.23	5.34	5.43	4.13	4.09	4.08
Fu-Ben-Hy	5.31	5.43	5.54	5.04	4.93	4.81

Equilibration period =2 h; Amount of resin =0.5g

Table 5 — Swelling (%) of resin in various solvents

Resin	Glacial acetic acid	Water	DMF	Dioxane	Alcohol	THF	Benzene	Acetone	Petroleum ether
Fu-Ben-GA	2.62	6.61	1.49	1.47	2.46	1.50	0.74	1.56	0.00
Fu-Ben-pHy	3.33	6.28	2.26	1.33	2.47	1.64	0.69	1.35	0.00
Fu-Ben-SA	2.74	6.66	2.89	1.87	2.87	1.57	0.93	1.39	0.00
Fu-Ben-Hy	1.77	6.24	1.13	0.84	1.49	0.81	0.61	1.03	0.00

resin increased with rise in temperature of equilibrium (Table 4).

On heating the resin, certain basic gaseous decomposition products were produced which neutralized a part of the acid during equilibration, thus giving apparently higher values for the anion exchange capacity of the resin. The decrease in the cation exchange capacity of the resin (Table 4) with an increase in the temperature of equilibrium was only due to loss of inorganic groups.

The behaviour of these resins in non-aqueous solvents is reported in Table 5. The decreasing order of porosity (polar solvents) for resins as exchangers was in the order: Fu-Ben-SA >Fu-Ben-GA >Fu-Ben-pHy >Fu-Ben-Hy.

References

1   Kondo H & Ishida S. *J Pharma Soc Japan*, (1922) 489, 979; *Chem Abstr*, 17 (1927) 1456.

2   Mains G H & Phillips M, *Chem Met Eng*, 14 (1921), 661.

3   Biswas M & Packirisamy S, *Indian J Technol*, 17 (1979) 485- 486.

4   Inczedy J. *Analytical Application of Ion-exchange* (Pergamon Press, New York), 1966.

5   Dalal A & Kapadia R N, *Indian J Technol*, 19(3) (1981) 127.

6   Kunin R, *Ion Exchange Resins* (Wiley, New York), 1958; pp 335; 337; 345.

7   Krishnaswamy N & Dasare B D, *J Sin Ind Res*, 21D (1962) 438.

8   Helfferich F, *Ion Exchange* (McGraw-Hill, New York), 1962, 85.

9   Dorfner K, *Ion Exchangers* (Ann Arbov Science Publishers, Michigan), 1972, 51.

10   Ghosh B K, Mahan A, Ghosh A K & Dey K A, *J Indian Chem Soc*, 57 (1980) 591.

11   Dasare B D, Gujjar K B & Krishnaswamy N, *Res Ind*, 13 (1968) 30.

Graft Copolymerization of Acrylonitrile Onto Hemicellulose and Its Effect on Paper Sheets

Aisha AA Soliman

Cellulose and Paper Department, National Research Centre, Dokki Cairo , Egypt

The ability of potassium permanganate to induce graft copolymerization of acrylonitrile onto hemicellulose (obtained from alkali extracted corn cobs holocellulose) was investigated. The graft yield depends on monomer and initiator concentration as well as reaction time and temperature. Chemical analysis of the reaction product of hemicellulose and acrylonitrile in the presence of potassium permanganate revealed that the potassium permanganate acted as an initiator for polymerization of acrylonitrile and as oxidizing agent for hemicellulose. The grafted samples were characterized by thermogravimetric analysis. The data obtained show that the thermal degradation of the samples obeys a first order reaction. The results further indicate that the activation energy increases with grafting. The kinetics parameters indicate that grafting increases the thermal stability of hemicellulose. Strength properties and water retention value of the paper sheets prepared from wood and bagasse pulp after addition of different amounts of native and grafted corn cobs hemicellulose were investigated, and the results discussed.

Introduction

Hemicellulose is a mixtures of low molecular weight polysaccharides which are closely associated in plant tissues with cellulose. Different methods have been developed for isolation of hemicellulose from plant materials[1,2]. The hemicelluloses in their natural state are generally considered to be noncrystalline. This is due to the heterogeneity of their chemical constituents, the presence of short side grouping, and in some cases branching. As the hemicelluloses are structurally related to cellulose, their reactions are very similar. The hemicelluloses form addition compounds at their hydroxyl groups, which also can substituted to ester and ether groups[3]. Ohtani and co-workers[4] studied carboxymethylation of hydrolyzed hemicellulose and starch, which are useful as builders for detergents. Others[5] studied the crosslinking, cyanoethylation, and hydrolysis of cellulose, starch, and hemicellulose to give products with different ion exchange capacities. Various studies were done for using the hemicellulose and oxidized hemicellulose as a binder in paper making[6,7].

Grafted hemicelluloses have extremely high water absorbances and therefore hold industrial promise for future, because when added in small amounts during paper-making it reduces the time and power required to soften and fibrillate fibers during mechanical action in water.

Few investigations, so far, have been published on the graft copolymerization of vinyl monomers onto hemicelluloses[8], in spite of the intensive investigations that have been done for various cellulosic materials and starch[9,10].

In this paper results of studies of graft copolymerization of acrylonitrile onto hemicellulose isolated from corn cobs using potassium permanganate as initiator for grafting, have been reported.

Experimental

Hemicellulose Preparation

Corn cobs were finely ground to 40-60 mesh and extracted with ethanol-benzene 1:1 for 6 h. The holocellulose was prepared using the acetic acid-sodium chlorite method[11]. The hemicellulose was then obtained from the holocellulose by extraction with 10%

sodium hydroxide for 20 h at room temperature and liquor ratio of 1:20. Then it was precipitated by acidification with 50% acetic acid to pH 4.5, followed by the addition of 3 volumes 95% ethanol. The hemicellulose was separated by decantation and solvent exchanged with 75% ethanol, 95% ethanol and ether, and dried under vacuum over calcium chloride.

Grafting

Using freshly distilled acrylonitrile (AN), the graft copolymerization was carried out as follows.

The required portion of aqueous solution of potassium permanganate of known concentration was placed in a glass- stoppered flask. The hemicellulose (lg) was introduced into the flask and the required amount of AN was immediately added, followed by 10ml 2N sulphuric acid. The volume of the reaction mixture was then adjusted so as to give a total volume of 50 ml. The flask was stoppered and shaken immediately and occasionally during the course of reaction. After the desired time, the reaction was quenched with a small amount of sodium thiosulphate. At this end, the sample was filtered on a sintered glass crucible, washed well with distilled water and dried at 60°C in an oven. The sample was then soaked in plenty of dimethyl formamide at room temperature for 24 h, followed by drying. The grafting yield percentage was determined from the values of the nitrogen content of the grafted samples by the kjeldhal method12.

Carboxyl Content

The carboxyl content (meq COOH/100g hemicellulose) was determined iodimetrically[13].

Thermal Analysis

The thermogravimetric analysis (TGA), the differential thermal analysis (DTA) for both native and grafted corn cobs hemicellulose were carried out by a Perkin-Elmer thermogravimetric analyzer TGA7, from 50 to 550°C. The rate of heating was adjusted to 10 K min^{-1}, and heating was continued to a constant weight in a stream of nitrogen.

Preparation of paper sheets

In all experiments, the softwood pulp and the unbleached bagasse pulp were beaten in a "Valley Beater" till 30° SR. This was followed by addition of native and grafted hemicellulose in presence of rosin

size and alum. The pH of the pulp slurry was adjusted to 5-5.5 by alum.

Paper sheets were prepared according to the German Standard Method.

Testing of paper

Tensile strength and burst strength were determined according to the German Standard Method 14. Brightness and opacity were determined by using a Carl Zeiss Elrepho Tester.

Water retention values were calculated according to the method described by Jayme[15].

Results and Discussion

The hemicellulose isolated from corn cobs was found to have the following analysis: 66% pentosan, 0.0% ash, and 5.16 meq. carboxyl content. The major sugar constituents of the hemicellulose were B (1-4) xylose, traces OF Arabinose and very little uronic acid.

The grafting of hemicellulose with AN using potassium permanganate as initiator was studied. Variables studied include monomer and initiator concentrations and reaction time as well as temperature.

Initiator Concentration

The effect of potassium permanganate concentration on grafting of AN onto hemicellulose is shown in Table 1.

The graft yield, expressed as percent nitrogen increases as the potassium permanganate concentration increases, reaching the maximum grafting with

Table 1 — Effect of potassium permanganate concentration on grafting*

KMnO$_4$ 0.1 N(ml)	%N	Carboxyl content M.E. COOH/100g Hemi	Increase in the -COOH content
0	0.00	5.16	0.00
1	0.47	75.40	70.24
5	1.30	79.00	73.84
10	1.27	60.40	55.24
20	0.68	47.30	42.14

*0.8ml AN,20ml 2N H$_2$SO$_4$,2g hemi., total volume, 100ml, room temp (20°C); duration, 1h

using 5ml $KMnO_4$. Further increase results in lower yields.

Previous reports[16,17] showed that radical formation in a polymerization system initiated by potassium permanganate in the presence of an acid seems likely to occur through reduction of Mn4+ to Mn^{3+} and/or Mn^{2+}. Thus during grafting of vinyl monomer such as AN to hemicellulose (hemi-OH) under the catalytic influence of potassium permanganate in the presence of an acid (HR), creation of free radicals in the system may be represented as follows :

$$Mn^{4+} + RH \rightarrow Mn^{3+} + H^+ + R^\cdot$$
$$Mn^{4+} + H2O \rightarrow Mn^{3+} + H^+ + Ho^\cdot$$
$$R^\cdot + H_2O \rightarrow RH + OH^\cdot$$

The acid and/or hydroxyl radicals attack hemicellulose to bring about hemicellulose macroradicals. The latter may also be formed according to the following reactions :

$$hemi - OH + Mn^{4+} \rightarrow Mn^{3+} + H^+ + hem\ i - o^\cdot$$
$$hemi - OH + Mn^{3+} \rightarrow Mn^{2+} + H^+ + hemi - o^\cdot$$

The capability of the hemi macroradicals to capture the monomer would determine the magnitude of grafting.

On the other hand, grafting would remain constant or oven reduced if the active sites on hemicellulose are combined to give a crosslinked hemicellulose or undergoes further reactions with agents rather than the monomer. Present work reveals that potassium permanganate acts as initiator for polymerization of AN and as oxidizing agent for hemicellulose under the conditions studied, but the rate of oxidation is higher at higher potassium permanganate concentrations till 5ml 0.1N $KMnO_4$ and further increase bring about lower yields. This is, indeed, obvious from the last two columns in Table 1. where the carboxyl content of the grafted product increases as the potassium permanganate concentration increases, up to 5ml $KMnO_4$ and after that the carboxyl content decreased.

Monomer Concentration

Table 2 shows the effect of AN concentration (based on weight of hemi.) on the graft yield, expressed as percent nitrogen.

It can be seen that the graft yield increases by increasing the monomer concentration within the range studied.The higher increase in grafting at higher monomer concentration could be explained if

Table 2 — Effect of acrylonitrile concentration on grafting*

% Volume of AN per weight of hemi	20	40	60	80	100
% N of the grafted product	0.95	1.30	1.55	1.66	1.69

*15 ml of 2N H_2SO_4, 7.5 ml $KMnO_4$, 1.5g hemi., total volume 75 ml., room temp.(20 °C), 1h.

Table 3 — Effect of reaction time on grafting*

Reaction time (h)	0.5	1	1.5	2	2.5
%N	0.97	1.30	1.31	1.01	0.69

*0.4 ml An, 10 ml 2N H_2SO_4 5 ml $KMnO_4$, 1g hemi. total volume 50 ml. room temp. (20 °C).

Table 4 — Effect of temperature of reaction on grafting*

Temperature of reaction °C	%N
20	1.30
35	0.66
50	0.63

*5ml $KMnO_4$ 10ml 2N H_2SO_4, 1g hemi., 0.4ml AN 1h. Carboxyl content of ungrafted hemi =5.16 M.E./100 hemi.

it is assumed that magnitude of association of the monomer with hemi. becomes significant at these concentrations. As a result the availability of monomer in the vicinity of hemicellulose macromolecules is greater thereby leading to higher grafting.

Reaction Time

Variation of grafting, as expressed as percent nitrogen with reaction time is shown in Table 3.

Increasing the reaction time from half an hour to one hour is accompanied by a significant increase in grafting.

Further increase in reaction time leaves the magnitude of grafting unaltered, indicating that a reaction time of one hour constitutes the optimal duration for grafting of AN onto hemicellulose using potassium permanganate as initiator under the conditions used.

Reaction Temperature

Table 4. depicts the effect of temperature on grafting of hemicellulose with acrylonitrile.

From Table 4, it can be seen that, the graft yield decreases by raising the reaction temperature from 20°C to 50°C. This decrease in the graft yield could
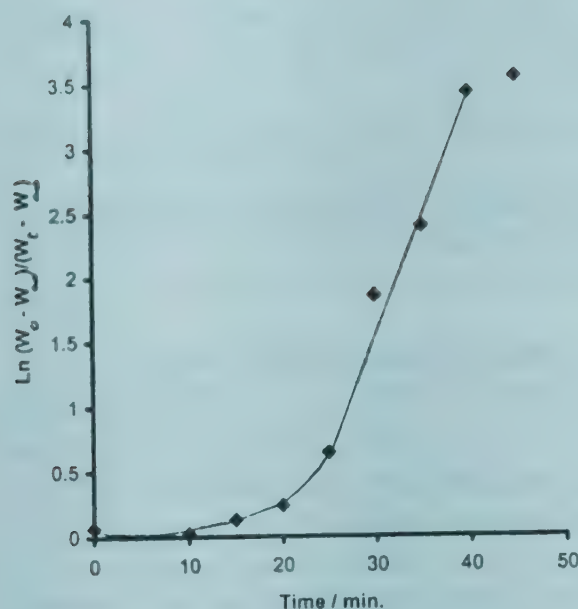
Fig. 5 — Plots of ln $(W_0 - W_\infty)/(W_t - W_\infty)$ against time for native cellulose
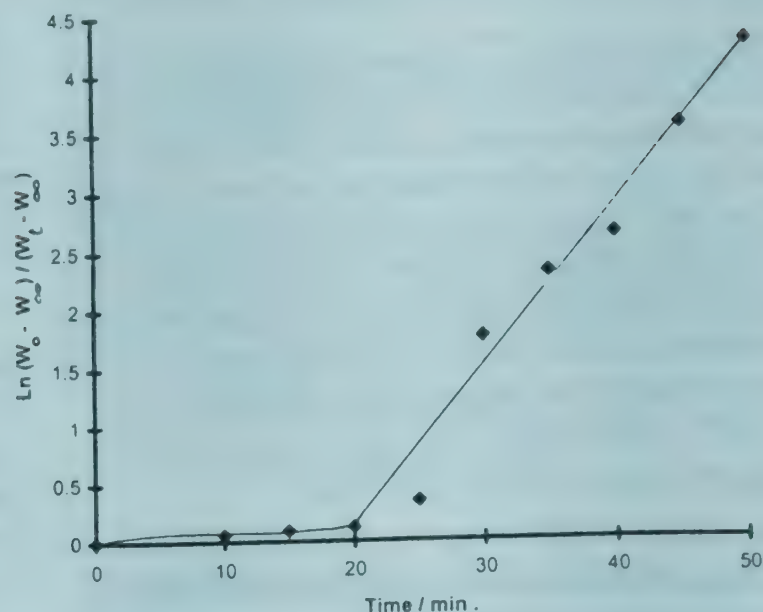
Fig. 7 — Plots of ln $(W_0 - W_\infty)/(W_t - W_\infty)$ against time for grafted cellulose (% N =1.55)
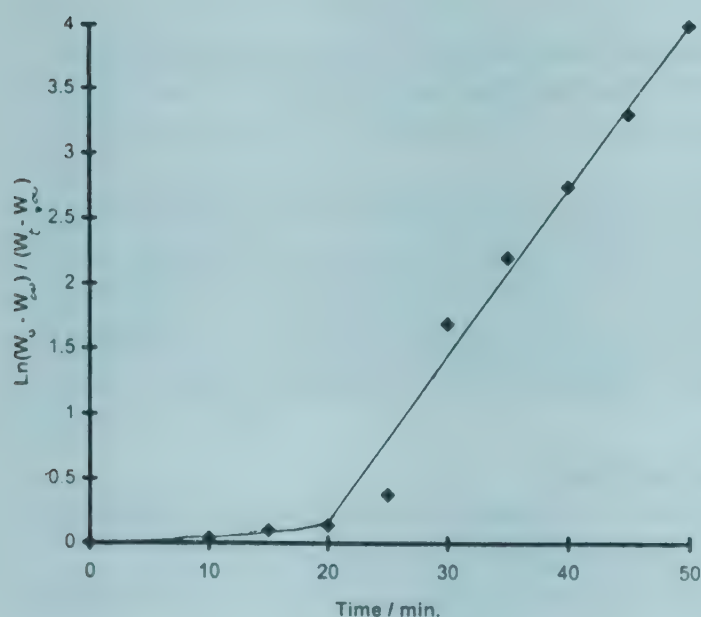
Fig. 6 — Plots of Ln $(W_0 - W_\infty)/(W_t - W_\infty)$ against time for grafted cellulose (% N =1.3)
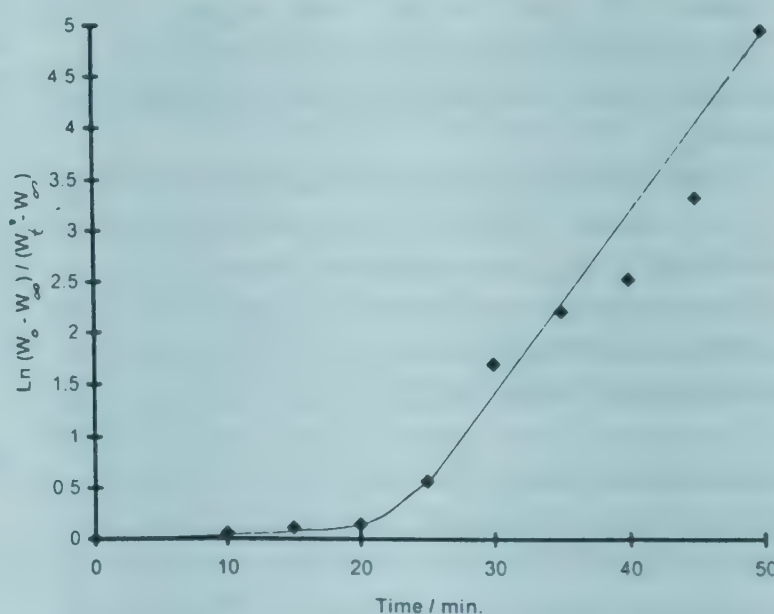
Fig. 8 — Plots of ln $(W_0 - W_\infty)/(W_t - W_\infty)$ against time for grafted cellulose (% N =1.69)

Properties of Hand Sheets

Properties of paper sheets prepared from beaten softwood pulp containing 1,2,4 and 5 % (g hemi/100g pulp) native and grafted hemicellulose at a pH of 5-5.5 (in presence of rosin size and alum) are given in Table 7.

It is evident from the table that 1 % added grafted hemicellulose represents the optimum addition at which the best improvement in breaking length, burst factor and water retention value was achieved than

1% native hemicellulose addition, the improvement being 24.7%, 51.6% and 29.86% respectively.

It is concluded that grafted hemicellulose resulted in lot of improvement in paper properties than native hemicellulose, and the best results were obtained at 1% grafted hemicellulose addition.

Remarkable improvement in printing opacity was noticed at 4% grafted hemicellulose addition, where the opacity increased by 16.6% than that of native hemicellulose addition.

dotherm, centered at 264°. The endothermal peak may be attributed to the formation and evaporation of some volatile pyrolysis products, while the exothermal one is due to the carbonization of these products[19,20].

Calculation of the activation energy

The data obtained by TG were analysed by the differential method used by Tang[21]. Assuming a first-order reaction for thermal degradation , the reaction rate constant, k, and the activation energy, E, in the main decomposition temperature region (150-350°C) were calculated from the relation.

$- dc/dt = kC$

where C is the concentration of the reactant, t is the time and k is the rate constant. If the concentration is replaced by the observed weight, W_t, then

$d(W_o-W_t)/dt = k[W_o-(W_o-W_t)] = kW_t$

where W_o is the original weight before heating, W_t the weight after heating for a time t. From the above.

$- \ln [W_o-(W_o-W_t)] = - \ln W_t = kt + constant$

But at $t=0$, $(W_o-W_t) = 0$, hence , the constant is equal to $-\ln W_o$, and therefore , $\ln(W_o/W_t) = kt$ If the amount of ash at the end of the heating is considered, then

$\ln[(W_o-W_\infty) / (W_t-W_\infty)] = kt$

Where W_∞ is the weight at the end of heating (ash). Plots of $\ln[(W_o-W_\infty) / (W_t-W_\infty)]$ against t give straight lines (Fig.5) indicating that the degradation follows a first-order reaction.

The activation energy was calculated by applying the Arrhenius equation[22] where

$\ln k = - E/RT$

that is

$-E = \ln kRT$

Where E is the activation energy, R is the gas constant and T is the absolute temperature.

The plots (Figs. 6,7 and 8) indicate that thermal degradation of grafted samples behaves in the same way as native hemicellulose. The TGA curves show the three parts, observed for native hemicellulose. It may be noted from the above figures that thermal decomposition of grafted hemicellulose generally starts at relatively higher temperatures, as compared with those for ungrafted hemicellulose. This may be explained by assuming that the grafting process in-

creases the molecular weight and results in a large chain than for native hemicellulose.

Table 5 summarizes the initial, maximum temperatures of the active pyrolysis, which are represented in the figures as T_1, T_2.

Table 5 also shows the percent volatilization at 250, 350 and 500°C which is used to indicate degradation rate and defined as a percent ratio of weight loss at specific temperature divided by the initial weight.

The values of activation energy for native and grafted hemicellulose are calculated from the Arrhenius equations. It is observed from Table 6 that the value of activation energy for grafted hemicellulose is higher than that for native hemicellulose.

Table 5 — Thermogravimetric analysis of native and grafted corn cobs hemicellulose.

Sample	Temperature of active pyrolysis °C		Volatilization (%)		
	Initial T_1	Max. T_2	250°C	350°C	500°C
Native corn cobs hemi	216	270	36	69	76
Grafted hemi %N = 1.3	240	269	17	48	53
Grafted hemi %N = 1.55	243	271	20	62	68
Grafted hemi %N = 1.69	225	300	29	60	67

(% volatilization =(weight loss at specific temperature / initial weight) × 100).

Table 6 — Activation energy values (E) and the reaction rate constant (K) of native and grafted corn hemicellulose.

Sample	$K(min^{-1})$	$E\ KJ_{mol}^{-1}$
Native corn cobs hemicellulose	0.185	1.429
Grafted hemicellulose %N =1.30	0.128	2.355
Grafted hemicellulose %N =1.55	0.136	2.286
Grafted hemicellulose %N =1.69	0.126	2.165
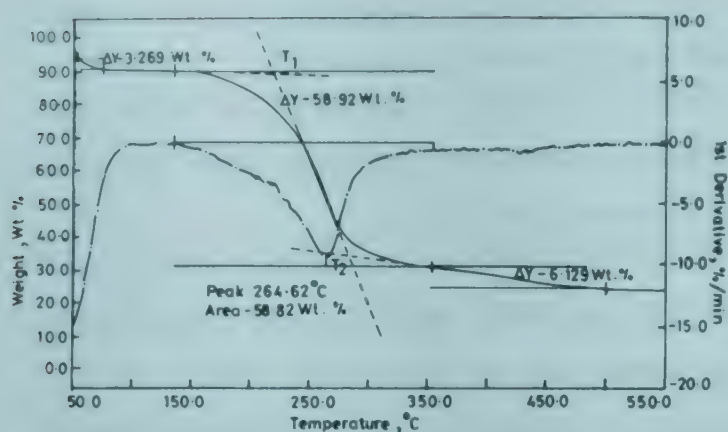
Fig. 1 — TG curves of native corn cobs hemicellulose
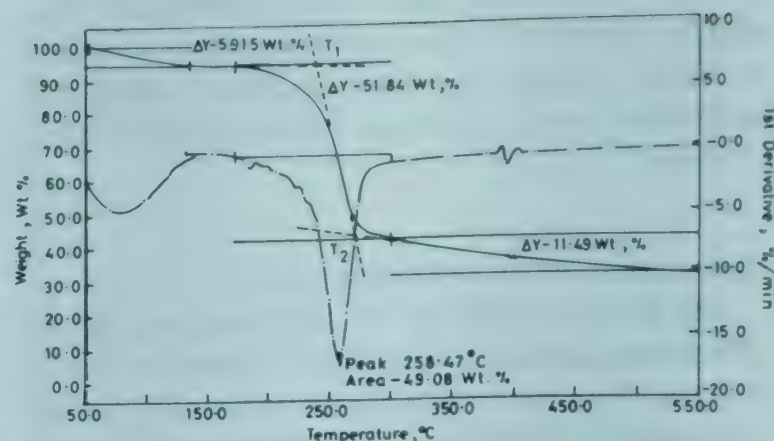
Fig.3 — TG curve of grafted corn cobs hemicellulose (% N = 1.55)
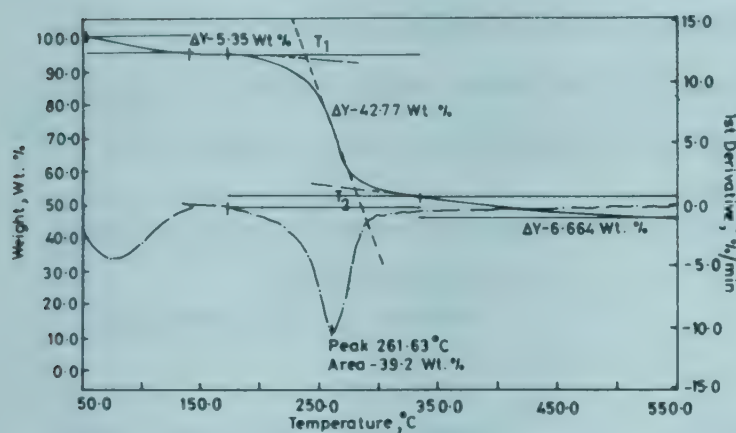
Fig. 2 — TG curve of grafted corn cobs hemicellulose (% N =1.3)
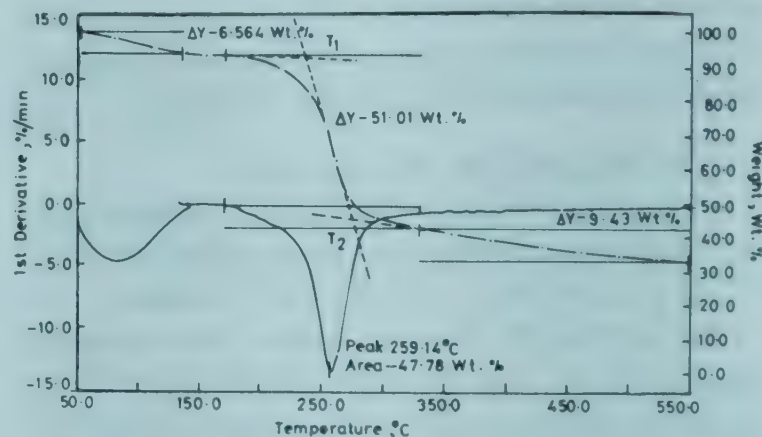
Fig. 4 — TG curve of grafted corn cobs hemicellulose (% N = 1.69)

be ascribed to the partial solubility of hemicellulose in acidic medium especially at high temperature.

Effect of Grafting on the Thermal Properties of Hemicellulose

TGA and DTA for native hemicellulose and grafted hemicellulose at different percentages are shown in Figs 1-4.

The TG curve may be classified into three parts. The first part from 50°C to about 150°C, representing the volatile materials and/or some residual absorbed water. The second part starts at about 150° and ends at about 350°C, representing the maximum weight loss due to the thermal degradation of the sample. The third part ranges from about 350°C to about 500°C and represents the carbonization of the products to ash.

The three parts may correspond to three steps suggested by Chatterjee[18], as representing the thermal degradation of cellulose. Thus, the first step :-

$A \rightarrow B_1$ Volatile product

The second step

$B_1 \rightarrow B_2 + L$

$B_2 \rightarrow B_3 + L$

$B_n \rightarrow B_{n+1} + L$

$\Sigma B_n \rightarrow B_{n+1} + L$

The third step :

$B_{n+1} \rightarrow$ Carbonization (ash)
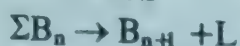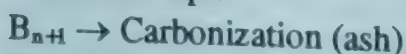
Where A denotes the initial molecule of hemicellulose

B_1 .... B_n are fragmental molecules, and L denotes the volatile product of decomposition.

The DTA curve of native hemicellulose, shows an exothermic reaction beginning at 135°C and ending at 354°C. This exotherm is interrupted by an en-

Table 7 — Influence of addition of native and grafted corn cobs hemicellulose on properties of paper sheets prepared from soft-wood pulp in presence of rosin size and alum.

Added amount of corn cobs hemicellulose (g hemi./100 g pulp)	Native hemicellulose					Grafted hemicellulose			
	0	1	2	4	5	1	2	4	5
Breaking length, m	2009	2023	2748	3243	3870	2523	2421	2488	3026
Burst factor	13.78	12.46	22.98	26.64	29.8	18.89	19.64	26.44	27.11
Tear factor	179	126.5	163	168	162	139	142	140	157.5
Brightness, %	85.3	82.7	84.3	81.4	76.4	79.3	80.7	67.1	83.6
Opacity, %	83.7	83.8	86.6	81.5	86.6	82.5	80	95	80
W.R.V %	167	144	180	164	185	187	160	172	161

Table 8 — Influence of adding native and grafted hemicellulose on properties of paper sheets prepared from unbleached bagasse pulp in presence of rosin size and alum.

Added amount of hemicellulose (g hemi./100 g pulp)	Native hemicellulose					Grafted hemicellulose			
	0	1	2	4	5	1	2	4	5
Breaking length, m	1587	1631	2148	2108	2116	1873	2106	1714	1696
Burst factor	10.9	9.87	13.48	13.8	15.95	11.98	14.35	12.59	13
Tear factor	44.6	46.8	34.76	34.5	62.08	49.16	53.85	43.97	49.46
Brightness, %	48.4	44.5	43.4	47	45.8	45.4	47.1	47.3	47.4
Opacity. %	91.5	110.6	104.8	94.7	92.4	101.3	96.4	96.8	98.3
W.R.V %	238	207	244	230	250	294	176	183	231

Influence of Native Grafted Corn Cobs Hemicellulose

Properties of paper sheets prepared from beaten kraft unbleached bagasse pulp containing 1,2,4 and 5 (g hemi./100 g pulp) native and grafted hemicellulose at pH of 5-5.5 in presence of rosin size and alum are given in Table 8.

There is a remarkable improvement in mechanical properties of paper sheets after addition of grafted hemicellulose with a small amounts (1g hemi./100 g pulp). The breaking length, burst factor and tear factor increased by a ratio 14.8%, 21.4% and 5% respectively due to addition of 1% grafted hemicellulose than 1% ungrafted hemicellulose. Brightness and printing opacity were also improved at this addition ratio.

WRV increased by 42% due to addition of 1% grafted hemicellulose than 1% ungrafted hemicellulose addition to bagasse pulp.

The increase in WRV can be attributed to the increase of hydrophilic groups of copolymerized monomer onto hemicellulose which generally originates by decreasing in the crystallinity of the hemicellulose structure, which take place during the grafting process, so that greater penetration of water into hydroxyl rich regions in permitted.

References

1 Wise L E, Murphy M & Addieco A A D, *Paper Trade J*, 2 (1946) 122, (1946) 35.

2   Sarkanen K V, *Pure Appl Chem*, **5** (1962) 219.

3   Sven A. Rydholm, *Pulping Processes*, (Interscience Pub., New York), 1965, 163.

4   Ohtani and Co-workers (Kao Soap Co., Ltd.). Jpn. Kokai 77 69, 990 (Cl.Co 8 B 11/12) (10 Jun. 1977). Appl. 75 / 146, 707 (9 Dec. 1975), 4pp.

5   Kuniak, Ludovit, Bennet, & Clifton Czech. pat. 161,464C (cl. Co7 C43/04) (15 Nov. 1975), Appl. 73/2,820 (19 Apr. 1973), 3pp.

6   El-Ashmawy A E, Mobarak F & El-Kalyoubi S, *Cellulose Chem Technol*, 10, (1976) 637.

7   El-Ashmawy A E, El-Kalyoubi S & Fahmy Y, *Cellulose Chem Technol*, **13** (1979) 77.

8   El-Shinnawy N A, & El-Kalyoubi S F, *Appl Polym Sci J*, **30**, (1988) 2171- 2178.

9   Hebeish A & Mehta P C, *Appl Polym Sci J*, **12** (1968) 1625.

10   Hebeish A, Abd El-Thalouth I, El-Kashouti MA & Abd El Fattah S H, *Angew Macromol Chem*, **1104** (1979) 101-108.

11   Whistler R L & Gaillard D E, *Arch Biochem Biophys*, **93** (1961) 332.

12   Vogel A I, *Quantitative Inorganic Analysis* (Longmans, London) 1961, 256.

13   Nabar G M, & Shenai V A, *Appl Polym Sci J*, **14** (1970) 1215.

14   Appleton Wisconsin *The Institute of Paper Chemistry*, *Institute Method No.* 411, 01 October 1951.

15   Jayme G, *Das Papier*, **12** (1958) 90.

16   Palit S R & Komar R S, *Polym Sci J*, **57** (1962) 85.

17   Nitra R, Mukherjee A R & Palit S R *Ind Chem J*, **3** (1965) 49.

18   Chatterjee P K, *Polym Sci J*, **6** (1968) 3217.

19   Shafizadeh P K & Bradburg G W, *Appl. Polym Sci J*, **23** (1979) 1431.

20   Hanna A A, Abd El-Wahid A & Abass M H, *Cellulose Chem Technol*, **11** (1984) 18.

21   Tang W K, U.S.Forest Service Research Paper, FPL 71, 1971.

22   Glasstone S, *Text Book of Physical Chemistry*, (Macmillan, London), 1962, 828.

Structural Changes on Cyanoethylation of Cellulose

Nahla A El-Wakil

National Research Centre, Cellulose & Paper Department, Dokki, Cairo, Egypt

X-ray diffraction patterns of differently substituted cyanoethyl cellulose are recorded. The crystallographic characteristics, namely crystallinity index (CrI), d-spacing changes, and extent of order variation have been estimated. The topography of fully substituted samples surface is explored using Scanning Electron Microscope. Such variations in the crystallographic parameters have been correlated with the degree of substitution.

Introduction

The presence of a large number of hydroxyl groups in cellulose molecules leads to the possibility of inter and intra-chain hydrogen bond formation. However, any physical or chemical changes induced within the fibres would be accompanied by concomitant changes in the internal structure of the fibre.

Partial substitution of the hydroxyl groups, resulted in the breakdown or alteration of the hydrogen bonds leads to various changes in the bonding system. On further substitution, specially with a bulky group such as the cyanoethyl group ($-CH_2-CH_2-CN$), a drastic change in the fibre structure could be obtained.

X-ray investigation on cyanoethylated cotton i.e. of lower DS was conducted by Conrad[1] in an attempt to improve the dyeability of the yarn, but no further information were given on the cellulosic fibres.

Moreover, literature survey showed no systematic investigations regarding this study, thus it is worthwhile to investigate the changes in the crystallography of the fibres as a function of the cyanoethyl content, DS.

Materials and Methodology

Viscose grade wood pulp, delivered from El-Nasr Company for Manufacture of Rayon, Bahteem, Egypt, was soaked for 20 h in water, shredded and allowed to dry in air. The sample obtained was analyzed to have : 94.70 per cent α-cellulose, 4.4 per cent hemicellulose and 0.05 per cent ash.

Acrylonitrile (Merck) was purified according to the method of Bamford[2].

Cyanoethylation

(i) To prepare a sample with DS less than unity, the cellulose sample was soaked for 30 min at room temperature in 1.5 M NaOH, then squeezed to remove excess alkali. Excess acrylonitrile (17 ml : 1 g fibre) was added and the mixture shaked for 3 h at room temperature. The reaction mixture was filtered, washed with hot water, then with ethanol, finally with ether and allowed to dry at 40°C.

The nitrogen content was estimated by kjeldhal method[3]. The sample was found to have DS 0.63 and is denoted as B.

(ii) For samples with DS between 1 and 2, the shredded wood pulp was soaked in 1.5 M NaOH for 45 min, squeezed from alkali and allowed to reflux with acrylonitrile at 76°C. for 15 min. A product of DS 1.4 was obtained, the sample is denoted as C.

(iii) To prepare a sample with DS more than 2, aging of wood pulp in 3 M NaOH solution for 3 days was first required followed by washing and drying. The reaction was completed according to whistler[4]. The crude sample was dissolved in acetone and the undissolved part was separated by centrifugation which posses DS 2 and is denoted as D. The dissolved one, obtained by evaporation of acetone, possesses DS 3 and denoted as E.

Fully substituted sample, E, was dissolved again in acetone and precipitated on water with stirring and filtered to obtain sample F. A reference sample (sample A) was obtained by soaking, for 30 minutes at room temperature, in 1.5 M NaOH. The sample was washed till free from alkali and air dried.

X-ray Diffractometry

Diffraction patterns of the reference sample as well as the other substituted samples were recorded on a Phillips diffractometer operated at 40 KV and 25 mA using Nickel filter and Cu Kα target. The diffraction patterns of the samples were recorded between 2θ value of 3-40 °C.

Electron - Microscope Study

Fully substituted cyanoethyl cellulose, samples E and F, were subjected to surface examination using scanning electron - microscope type "nanolab 7 ". The samples were previously coated with gold using " Sputter coater S 150 A ".

Results and Discussion

Figure 1 represents the X-ray diffraction pattern of the investigated samples A-E; it reveals that diffraction pattern of the cyanoethylated samples having DS 0.63, sample B, showed a little change in the crystal structure. Furthermore a rapid decrease in the height of the stronger 002 interference at 2θ = 23.2°C, can be noted for sample C, as previously observed by Segal[5] which posses DS of 1.4. Upon further substitution, this reduction increases and reaches its maximum at DS 3 (sample E). The doublet interference observed in sample A at 2θ =14 and 16 ° has disappeared in the diffraction pattern of cyanoethyl cellulose of DS 1.4 (sample C) with its peak diffused and appeared at 2 =θ 10°. This phenomenon is observed in sample D as well; whereas it is some what more distinct at the higher substituted sample DS 3, that obtained from acetone solution by evaporation (sample E). However, a slight decrease in the height of this diffraction was observed for sample F; which was obtained from acetone solution by water precipitation. This may support the idea of Sefain *et al*[6] that at higher substitution, crystallization in new planes may occur. The crystallinity of the fully substituted sample is dependent upon the method of preparing the sample from acetone solution.
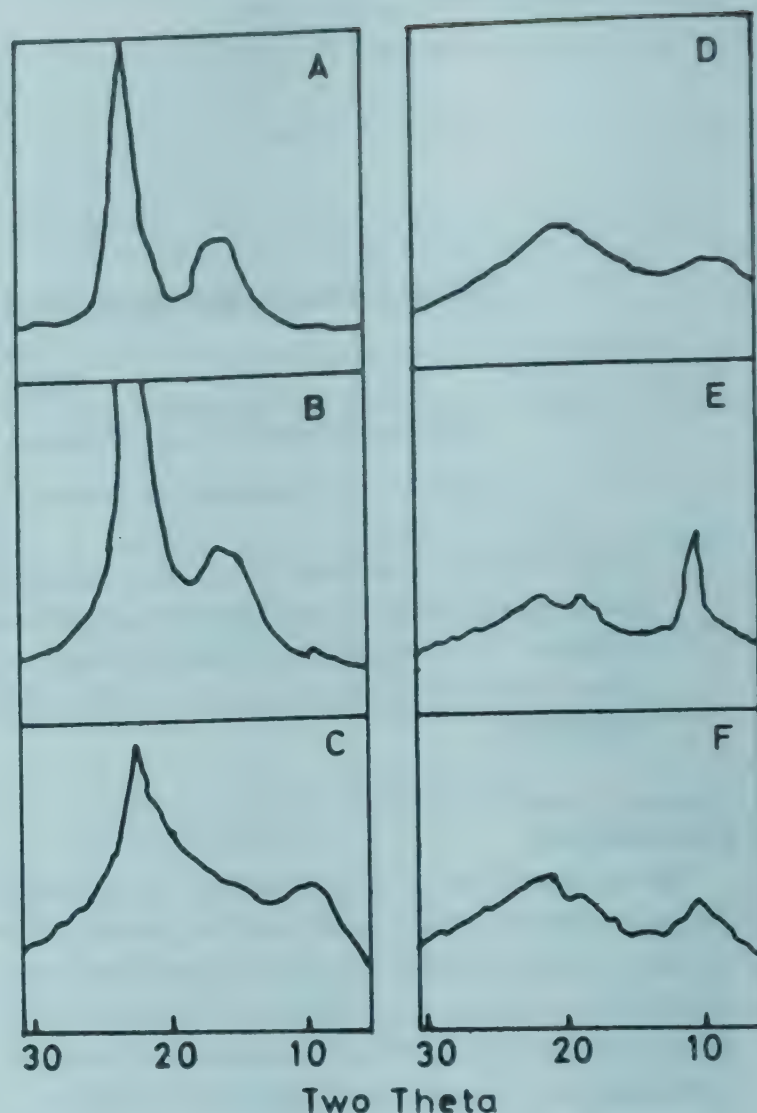
Fig. 1 — X-ray diffraction patterns of samples A-F

Changes in the Degree of Order

Since the peaks were originally scanned equatorialy, the area under the peaks will depend upon both the orientation and the total number of the diffracting planes. However, since the scanning was carried out using the disc technique, the orientation factor will be neglected and the changes in the total area under the equatorial peaks can be taken as a measure for the destructive variation in the degree of order resulting from the progressive substitution of the hydroxyl groups by the cyanoehyl ones. It was found reasonable to represent the changes in the degree of order for the natural polymer by the crystallinity index[7]:

$$C r I = \frac{I_{(002)} - I_{(18^\circ)}}{I_{(002)}}$$

The results of computation of the crystallinity index of the investigated samples (A-E) were tabulated in Table 1. It is evident that during substitution of the hydroxyl groups by cyanoethyl ones, DS 0.63,

Table 1 — Crystallographic characteristics of cyanoethyl cellulose						
Sample	A	B	C	D	E	F*
DS	0	0.63	1.43	2.00	3.00	3.00
Crystallinity index CrI	72.01	78.02	74.25	73.81	58.82	63.83
2θ value in degree (002)	23.2	23.0	22.8	20.3	21.6	21.8
d-spacing Å	0.1954	0.1970	0.1987	0.2219	0.2091	0.2073
h h w (arbitrary unit)	1.4	1.9	3.7	8	9	7.5

*Precipitated with water; h h w — half height width
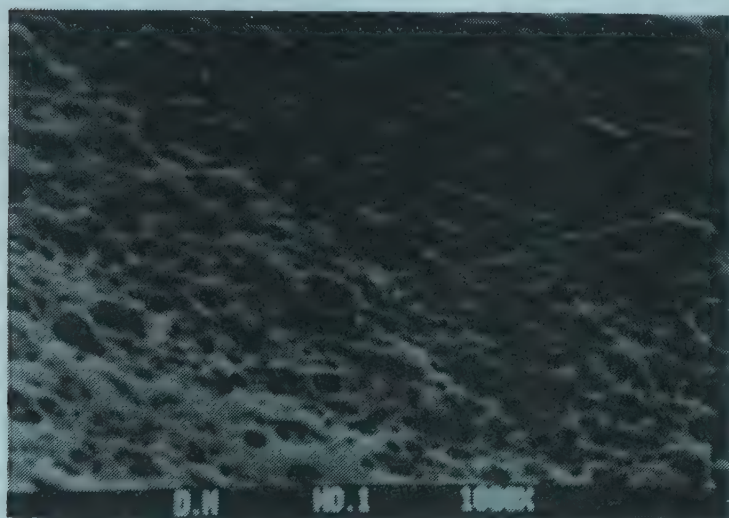
Fig. 2 — Cyanoethyl cellulose after solvent evaporation

the crystallinity index increases firstly which may be ascribed to some dissolution in the non- ordered part of cellulose during alkali pretreatment step. Successive introduction of cyanoethyl groups produces disordering into the fibres due to the possible loss in fibre structure upon the substitution above DS 1.1[1]. The effect of the method of recrystallization of the fully substituted samples (DS 3), once by evaporation of acetone and another by using water as a precipitant, on the diffraction pattern was clearly shown in samples E and F. Recrystallization from acetone produced a pale yellow film having a diffraction pattern included in Fig. 1 (sample E). But on using water as precipitant, a white fibre-like sample was obtained having the diffraction pattern occurred in sample F. Expectedly, evaporation of acetone causes reordering of the crystals that give a diffraction peak in the 10l and 10l̄[6] directions and a more distinct crystallization was obtained.

On precipitation of cyanoethylated solution with water, a more or less random arrangement would be obtained.

Changes in the d-Spacing

Determination of the changes occurred in 2θ angle which reflect changes in the d-spacing as a result of successive substitution are collected in Table 1. It is clear that, except for samples E and F, by successive substitution a shift of the position of 2θ angle of 002 peaks to a lower 2θ angle was obtained indicating an increase in the d-spacing. It seems possible to postulate that, introduction of the bulky groups into the structure accompanied by an alteration of the H-bonding system, either by rupture or substitution led to an increase in the d-spacing.

Changes in the Extent of Order

Peak broadening is mainly affected by two structural factors crystallite size and lattice strain. Under certain circumstances it is possible to differentiate between these factors[8], however since the higher equatorial orders are absent in the cellulose product, such analysis is not possible, thus the variation in the half height width of the peak as a measure of the changes in the extent of order taking into consideration that the half height width is inversely proportional to the extent of order i.e. crystallite size; such changes are tabulated in Table 1. It is clear that the extent of order decreases with successive substitution of the hydroxyl groups with the cyanoethyl ones. The decrease in the extent of order is comparable with the decrease in the crystallinity index of the sample which support the idea that, cyanoethylation produces disordering in the fibres and as the degree
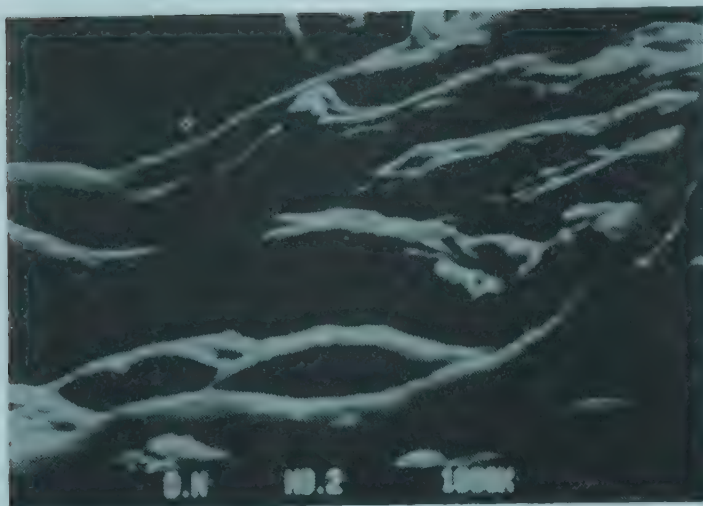
Fig. 3 — Cyanoethyl cellulose after water precipitation
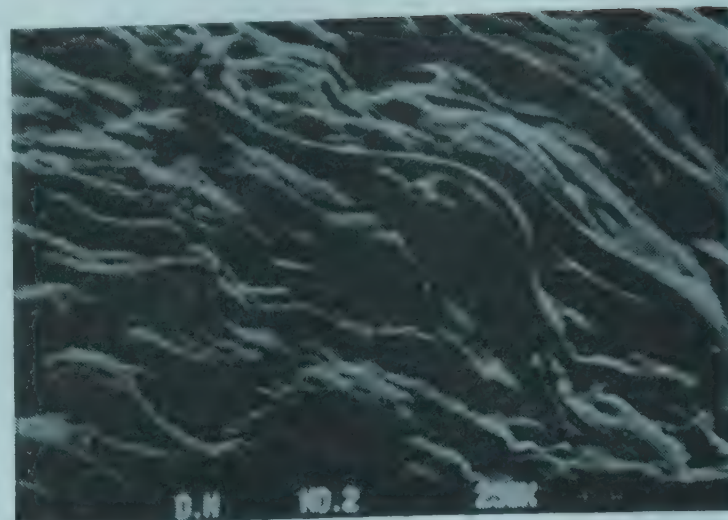
Fig. 4 — Corrugated surface of cyanoethyl cellulose after water precipitation

of substitution increases and the extent of order decrease.

It should be mentioned here that all this discussion concerns the 002 diffraction plane. However the destruction of 002 plane observed on increasing the substitution may be due to a new crystallographic plane formed in 101 and 101 planes[1].

The micrograph shown in Fig. 2 shows an uneven film surface of the cyanoethyl cellulose formed after solvent evaporation forming pores within the fibres. On the contrary cyanoethyl cellulose precipitated by water addition show flat ribbons (Fig. 3) which give some sort of fibre shaped, gathered in an irregular array with more or less uneven corrugated surface (Fig. 4). These flat ribbons formed coincide with the finding obtained by Compton et al.[9] who examined the cross section of the cyanoethyl cellulose using optical microscope.

Conclusions

Cyanoethylation of cellulose affects the crystallographic characteristics of the samples.

As the degree of substitution increases, disordering of the fibres increases with occurrence of a new diffraction pattern at higher DS in some crystallographic directions, i.e., at $2\theta = 10°$

References

1   Conrad C M, Stanonis D J, Harbink P & Creely J J, *Textile Res J*, 1 (1960) 339.

2   Bamford C H & Jankins A D, *Proc R Soc (London)*, **A216** (1953) 313.

3   Vogel A I, *Quantitative Inorganic Analysis* (Low and Brydon Printers Ltd.) 1962, p 256.

4   Whistler R L, *Methods Carbohyd Chem*, 3 (1962) 317.

5   Segal L & Conrad C M, *Am Dyestuff Reptr*, **46** (1957) 637.

6   Sefain M Z, Naoum M M, Fadl M H, El-Wakil N A, *Thermochim Acta*, **231** (1993) 257.

7   Segal L, Creely J J, Martin A E & Conrad C M, *Textile Res*, **29** (1959) 786.

8   Alexander L E, *X-ray Diffraction Methods in Polymer Science* (London, Wiley Inter Science) 1969, p. 423.

9   Compton J, Martin W H & Barber R P, *Textile Res J*, (1955) 58.

BOOK REVIEWS

The MIT Guide to Science and Engineering Communication, by James G Paradis and Muriel L Zimmerman (The MIT Press, Cambridge, Massachusetts, 02142) 1997, pp 290; Price: $ 27.50 [ISBN 0 262 16142 7]

Communication is an essential element of any profession. In Science and Engineering, the communication process itself helps to form knowledge and make it available to S&T workers, policy makers, funding agencies, industry and a wide spectrum of other users, leading to its utilization and further advancement.

Scientists and Engineers, starting from taking up a project to its successful accomplishment, have to communicate at various levels, to different target audience which may be co-workers, peers, sponsoring agency, industry, etc. Good communication undoubtedly plays an important role in promoting the career of S&T personnel.

The MIT Guide to Science and Engineering Communication comprises 18 chapters which deal with all the four facets of S&T communication, viz. written, oral, graphics and electronics, as crucial and inseparable entities. The book takes into account the fact that science writing is today a group rather than a solitary activity, and discusses specific processes and forms that will help individuals create documents. The authors, from their long drawn experience of teaching college students and science professionals, have included numerous realistic examples making the reading interesting and effective.

The first chapter describes how important good communication is to a successful career in science. Pointing out that the written communication can be analyzed to minute detail, it stresses on using a clear, consistent and accurate language. It also emphasizes on proper planning and recording of the information collected or generated, for this forms the basis of writing. Recording of the information should preferably be done using digital technologies. The advantages being easy storage and retrieval of the data, and its reformatting to meet the interest and needs of different type of readers.

The second chapter speaks about defining the audience and aims, and tailoring the documents by adjusting coverage, organization and language keeping the needs of the target audience in view. The chapters that follow address such topics as drafting documents; revising these for organization and style; developing graphics; conducting meetings of the people from various departments/groups associated with the project who will need to write and review the drafts that will be consolidated to produce the final document; writing memos, letters and electronic mail; writing proposals for seeking funds, sponsorship, etc.; writing progress/final reports and journal articles; citation and reference styles; preparing documents/visuals for giving instructions and procedural details (e.g. instrument manuals, warning signs and accident prevention tags)' and document design.

The advancements in digital techniques have revolutionized the field of communication to the extent that people have started speaking in terms of a paperless future. Today one can prepare an electronic document composed of text, graphics, video images and audio, in an 'intelligent' or 'interactive' mode. The chapter on Electronic Text discusses writing an electronic document, designing for the computer screen, hypertext, multimedia, and World Wide Web.

A major problem faced by the fresh research workers is how to search the literature. This problem is addressed in a chapter on Strategies for Searching the Literature, which throws light on subject, snowball, citation, star, comprehensive database and current awareness searching techniques, and also mentions about a few of the prominent information venders and their services.

The book contains a chapter on how to make oral presentations more interesting and communicative, and another on preparing the job search documents.

The authors have made a good attempt to bridge the gap between a novice and a skilled professional. The book is recommended for research fellows, scientists and other professionals engaged in S&T information generation and communication.

B C KASHYAP
National Institute of Science Communication,
New Delhi 110012

Supercritical Fluid Extraction Technology for Natural Products, edited by R C Maheshwari and S N Naik (Omega Scientific Publishers, New Delhi 110 024) 1996, pp 164, Price: Rs 450/=, $ 45.00 [ISBN 81 85399 360 (hb)]

Currently, as compared to in the past, a shift is taking place in favour of natural renewable raw materials in view of the harmful effects associated with synthetic compounds, such as their side effects, persistence and pollution of environment. The conventional methods used for the extraction of natural raw materials for isolating pure compounds are not free from certain drawbacks. Many artifacts are found not only during soxhlet extraction or extraction by solvents at room temperature but also during the isolation of pure compounds from these extracts by column chromatography, the reason being that most of the natural products are sensitive to heat, sunlight, and air. Supercritical fluid extraction using carbon dioxide has emerged as a promising technique. When a solute molecule is thrown into the supercritical fluid (SFC) and if the solute-solvent interaction is larger than the solvent-solvent interaction, the solute molecule may be surrounded by the solvent molecules, forming a cluster because the attractive potential energy around the solute molecules is larger than the average kinetic energy of the solvent (super-critical) molecules. Clustering around a solute molecule is now considered to be a major cause of enhanced solubility in SFCs.

Among various supercritical fluids, carbon dioxide is the most widely used substance, especially in SFE because it is inexpensive, non-toxic, non-inflammable, and has relatively low critical temperature (31.1°C), and pressure (79.2 atmos). In capillary supercritical fluid chromatography and/or analytical SFE; ammonia, xenon, hydrocarbons, and nitrous oxide have been examined in supercritical mobile phases and extraction media. Advantages of this technique are: the extract is entirely free of any

solvent, the product faithfully represents the original material, There are no leftovers in the final product, and the residues and the chemicals present in the extract do not undergo chemical changes, such as thermal, photochemical, esterification, hydrolysis or oxidation.

The book under review is compilation of research and technical papers presented at the symposium on "Supercritical Fluid Extraction Technology of Natural Products", organised by the Centre for Rural Development and Technology, Indian Institute of Technology, Delhi in association with "Essential Oil Association of India". The book aims at presenting the current state-of-art in the extraction of natural products with SFC and to understand fundamentals of SFC theory and process application.

Most of the papers in this book deal with the recent achievements in instrumentation and applications to natural products, the potential advantages of SFCs as extraction media and as a mobile phase in chromatography owing to their higher solvating power than the normal liquid (i.e. liquid at room temperature and atmospheric pressure), their inertness, availability in highly pure state, non-toxicity, non-corrosiveness, non-inflammability and inexpensive nature.

Although the carbon dioxide-High Pressure Technology has been in commercial application at industrial scale for more than 20y but considering the world market for fragrance compositions, aroma chemicals, essential oils, and other natural products, the knowhow and design of adequate equipment as well as proper details of engineering are necessary. Some of the papers in the book deal with the design of equipment. Optimum operating conditions for extraction with supercritical gases using continuous thermodynamics have been evaluated for process-design calculations. Energy requirements on the basis of relevant thermodynamic calculations have also been estimated for supercritical fluid extraction processes. Further, for estimating mass transfer rates in SCFE process, generalised equations in terms of dimensionless have been used to predict the values of transport co-efficient. A paper on extraction of much talked about and potential source of pest-control agent of botanical origin, *Azadirachta indica*, commonly known as *Neem* with supercritical carbon dioxide will open a new era for the isolation of azadirachtin-rich fraction, a chemical responsible for

the pesticidal properties of neem and other such photo-and thermal labile natural products. Removal of undesirable components from edible oil using SFE is another useful finding of the symposium. There are many more valuable papers which form apart of this book.

On the whole the book has covered most of the aspects related to SCFE technology and will be a good acquisition for libraries, for the researchers working in the areas of agrochemicals, pharmaceuticals, and perfumery materials of natural origin, students, and industrialists in the country.

D B SAXENA
Division of Agricultural Chemicals,
Indian Agricultural Research Institute,
New Delhi 110 012, India

SCI-TECH UPDATE

India joins the team to build world's largest radio telescope

Radio astronomers from India are taking part in an ambitious project to build the world's largest radio telescope along with those from Australia, Canada, USA, Netherlands, and China. The astronomers hope that this telescope will enable them to image ever fainter and more ancient galaxies. It would combine images from 34 detectors spread out over a square 250 km on a side.

The Square Kilometre Array Interferometer (SKAI) will have a total area of 1 km square, 75 times more than the biggest comparable radio interferometer, the Very Large Array in New Mexico. It will enable astronomers to see even further than the Hubble space telescope because of its special design.

A Dutch-Australian team has provided an unusual or unconventional design in which each detector would consist of hundreds of small linked radio receivers. They would detect specific objects by measuring phase differences which depend on the radio sources position in the sky. The participating teams believe that they can begin construction by 2005 [Science, 276(1997)1037]. ❑

DSRM

New environment friendly method for melting ice on roads

In areas where the roads are covered with heavy snow, winter driving becomes difficult and is a concern for industry and local governments. The usual methods to clear the roads for traffic flow are snow ploughing and removal, spreading salt, and building and maintaining equipment for melting snow on streets and sidewalks.

In Japan, the most popular method for melting snow is to sprinkle ground water over the roads. Another method is to pump groundwater through buried tubes installed under roads and then return the water to the underground aquifers. In areas that are extremely cold or that lack an adequate supply of ground water, electric heating cables or boilers burning kerosene or natural gas are used for melting snow. These systems consume precious fossil fuels but also produce large volumes of carbon dioxide pollution.

A new system that overcomes these draw backs has been developed by the National Institute for Resources and Environment, under the Ministry of International Trade and Industry's Agency of Industrial Science and Technology, called the Gaia Snow-Melting.

System in conjunction with several private companies. This system uses both the universally distributed low-temperature heat retained in the ground and the heat of the sun during the summer.

The first Gaia Snow-Melting System was constructed in Ninohe City, Iwate Prefecture, in 1995 and was successfully implemented.

The Gaia snow-Melting System (GSMS) uses a Downhole Coaxial Heat Exchanger (DCH6) to extract heat from the ground (Fig.1). In addition it uses several other technologies developed in collaboration with Mitsui Engineering and Ship-building, Kubota, Koken Kogyo, etc. Bulk of the heat used in GSMS is drawn from water from depths of 100-
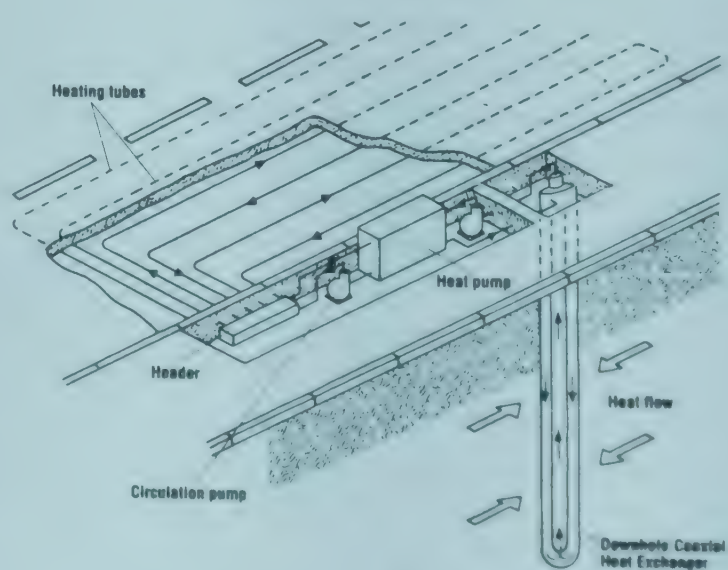

Fig.1

200m with 10-20 degree Celsius. This water is passed through heat pump to raise the temperature. This in turn is used to heat an antifreeze liquid that circulates through distribution pipes under the road, thereby heating the road surface to melt the snow.

During the summer months, the sun's heat raises the temperature of the ground in which the heating tubes are laid (about 10 centimeters under the road surface) to between 40 and 50 Celsius. This heat is absorbed by the circulating antifreeze and returned to the DCHE where it warms the surrounding ground, which acts as heat storage site. In the winter, this heat combines with the geothermal heat to melt snow.

The GSMS system was tried in Ninohe city. The area covered by the snow melting system is 4m wide and 65m long covering a total area of 266 m^2. There DCHEs were used, each 9 cm in diameter and 150m deep. A 15-Kilowalt electric heat pump was also used. The heat supplied to the heating tubes is approximately 50 kilowatts. The system is controlled by a newly developed operation control system that automatically kicks on when there is snow or ice on the road.

The GSMS was found to be efficient and economical. It consumed only 14% as much electric power per unit area as Ninohe's conventional electric cables system. This is due to (i) use of natural heat energy and (ii) built-in control systems regulating the number of hours the snow-melting system was kept active during the winter reason. The running costs were only 26% of the electric heating cable system. However, the cost of construction arising from the need to bore a hole for the DCHE is a bit high and a cheaper method for the same has to be developed [*Look Japan*, November 1996, pp.28-29].   □
DSRM

Corrosion assessment techniques to reduce excavations in oil pipe lines

The trans-Alaska pipeline stretches from the northern settlement of Prudhoe Bay on the Arctic Ocean, across the Brooks, Alaska, and Chugach mountain ranges, to Port Valdez on the state's southern coast. Half of the 799-mile pipeline is buried and half rests on supports above ground, to avoid permafrost melting that can lead to structural and environmental damage. Up to two million barrels of crude oil are pumped through the four-foot diameter pipe-

line daily, cooling from an average temperature of 120F at Prudhoe Bay to about 70 at Port Valdez.

The South West Research Institute (SWRI), San trans-Alaska pipeline corrosion-assessment digs in earlier 1996. All three digs were located on the Saggavanirktok River, between 75 and 80 miles from Prudhoe Bay. Most excavations to assess damage to the pipeline are conducted during the winter season, when river bottoms through which the pipe runs are frozen. Observations made during the trip are aiding development of improved methods of modeling complex failure modes in large pipelines.

The Alaska pipeline has experienced anticipated normal levels of settlement/or corrosion. An internal measurement device called "smart pig" identifies the settled areas as well as to identify areas of external corrosion in the pipeline. But this device does not necessarily indicate how the settled or corroded areas affect pipe strength. Settled portions of pipe may need to be excavated and leveled to guard against wrinkling of the pipe wall, and corroded areas may need to be excavated and sleeved to guard against rupture. Currently, Institute engineers are engaged in the development of analytical techniques and experimental tests to help extend the service life of the pipeline.

Because substantial cost and environmental risk are involved, quantitative rather than just experimental procedures are needed for determining whether or not to excavate.

Alyeska Pipeline recently conducted experimental and analytical studies to understand pipeline behavior. One result of these studies is the Shell Analysis Failure Envelope (SAFE) computer program developed by SWRI. Using this program, the safety of corroded pipe can be assessed and a decision made regarding whether to excavate a specific corroded area and whether to add a sleeve to the exposed area.

The current and proposed work for Alyeska Pipeline consists developing a suitable experimental and analytical data-base for the definition and calibration of SAFE engineering calculations to predict the wrinkling capacity of a corroded and settled pipeline section.

Institute researchers have formulated a combined experimental and analytical approach to provide a comprehensive wrinkling calibration database. Full-

scale experiments will be conducted to provide a failure point for the database and to allow the qualitative comparison of experimental and finite element simulations of the pipe tested.

A total of nine data points, in addition to data from a representative test case, are required to provide a comprehensive database for calibration of engineering calculations. In addition to the recently completed representative test case, a minimum of three additional full-scale experiments have been proposed for 1997. Using the SWRI pipe test facility, sections of 48-inch diameter pipe will be evaluated under combined pressure, axial, and lateral loading conditions representative of those in arctic regions. These conditions will concentrate bending deformations within the thinned region at the test specimen center. The thinned region is machined to a reduced wall thickness that represents a general corrosion defect. For each experiment, a single test parameter such as applied load or thinned region size will be perturbed from the representative case.

An SWRI internal research project has produced an improved analytical procedure that will be used for the SAFE finite element test simulations. This procedure, which differs from corroded pipe simulations performed previously at SWRI and elsewhere, employs finite strain shell elements in a three-dimensional model of the pipe, as well as an advanced plasticity material model, to achieve wrinkling of the pipe wall in the thinned region. Initial phases of the project focused on implementing the material model in ABAQUS and validating the procedure through a comparison with tension and compression mechanical tests of pipe material samples. The analytical procedure has been employed successfully to simulate the representative test case, thus ensuring the validity of the approach and its applicability to the Alyeska Pipeline test program, as well as to other pipeline safety investigations. [*Technol. Today*, South West Res Inst., Antonio,**17**(3)(1996)10-12]□

DSRM

New highly accurate method for sewer inspections

Current inspection techniques for maintenance of sewer system suffer from several drawbacks for accurate condition assessment of old underground sewers. The prevalent methods are able to provide subjective assessment only. They are unable to reliably detect defects and provide information needed to monitor progressive deterioration—an important issue in preventing sewer collapses. Any method that predicts an impending collapse of a pipeline is welcome and can result in cost savings for water authorities. Apart from financial benefits, that will have environmental ramifications as usually damage of adjacent non sewer assets is involved, polluting the environment with sewage overflow and seepage to ground water supplied. Of late, in the light of litigious environment, these risks are to be taken cognizance of and minimized.

A joint project with Melbourne 'Water and the Australian CSIRO establishment has designed a new system using a combination of robotics, machine vision and artificial intelligence to examine and assess automatically underground sewers called, the Pipe Inspection Rapid Assessment Technique (PIRAT), it incorporated these new technologies to provide for a new level of accuracy in sewer investigations.

A CCTV-based assessment is presently in use for underground sewer inspections, but it is error prone and subjective, particularly with inexperienced operators. Some defects are very hard to be detected and the method makes high demands on the skill and concentration of the operator.

In contrast, PIRAT provides a reliable quantitative assessment of sewer condition. It is based on continuous and detailed measurement of the internal geometry of the sewer. The geometry data are analysed automatically to detect, classify and rate defects and the results are presented in an inspection report.

The main components of PIRAT are the technology to measure surface geometry and the condition assessment software. The former came from the Division of manufacturing and the latter from the Division of Building, Construction, and Engineering, both of CSIRO.

The system consists of an in-pipe vehicle which carries scanning equipment through the sewer and a mobile control room which houses data analysis and control equipment. Once deployed, the complete system is controlled by the computer.

A laser scanner is used in drained pipes and a sonar scanner is provided for flooded pipes, with data being transmitted at up to 400 Mbits per second between the in-pipe vehicle and the control room.

PIRAt enables quantitative assessment of the sewer condition, with sewer geometry established from multiple cross-section as the scanner is moved along by the in-pipe vehicle.

The interpretation system uses Artificial Intelligence (AI) techniques to automatically identify, classify and rate pipe defects.

The software is designed to process the radius data, up to 100,000 readings per metre, to produce condition assessment report. A Management Information System (MIS) allows further analysis of the results via a graphical user interface.

The project has matured from laboratory design and testing to field experiments. it is tested over a 4 km of 600 mm sewer in Melbourne and its performance was found to be superior to CCTV[*INSIGHT*, **39** (1) (1997) 9].

        ❑

DSRM

New technology boosts mass storage

Developed first at the Stanford University and subsequently at Digital Equipment Corporation and Quantum Corp., a new technology called Near Field Recording (NFR) technique that combines the magnetic disk and magneto-optical technologies may offer 10 times the capacity of hard disks available now at comparable speeds and costs.

NFR devices employ media platters that are similar to those in a hard disk as well as a low flying read/write head modified from those of hard disks. The head includes optical elements such as magneto-optical head and a solid immersion lens (SIL). The SIL enables each bit of cell data recorded on to the platter to be much smaller than with hard disk or magneto-optical technology, thus allowing more data on a platter: 12 Gb/sq in versus a typical hard drives' 1.2 GB.

The first NFR drives which may come into the market by spring of 1998 may offer 20 GB of storage in one platter designs. These will be ideal for use in work stations and as network servers. The drive will be available in both fixed and removable formats and what is more, will fit in standard 5.25" bays [*PC Mag*, 16 (8) (1997) 9].

        ❑

DSRM

Device to detect volatile organic compounds in workers

The Pacific Northwest National Laboratory (PNNL) in Richland, Washington, in conjunction with the Batelle Memorial Institute in Columbus, Ohio, is developing a device to screen workers for any of over 150 volatile organic compounds (voc) present in the breath. The Exposure-to-Risk Monitor System (E$_2$R) can provide breath analysis readings every 1.5 s which is considerably faster than conventional breath analysis systems that provide readings once every 20 min or so.

The E$_2$h system originally conceived and built at Batelle

was refined at PNNL by adding risk assessment algorithms and toxicology models.

The models are based on toxicologic studies in animals from which the data are extrapolated to humans. Thus the E$_2$R not only measures the level of volatile chemical in the individual's breath, but also can backtrack to determine the dose to which the worker was exposed and can use the toxicology models to calculate potential adverse effects from a given level of exposure.

The system refined at PNNL has (1) a data point every 1.5 s for any individual, (ii) the readouts are in real time, and (iii) the analytic process is done on the spot and provides an accurate measure of the toxins present and the probable dose to which the worker was exposed. Workers' exposure to industrial chemicals is often measured by air monitors or sensors they wear. The E$_2$R system measures workers individually (unlike the systems that assume all workers react similarly to the same exposure to a toxic chemical) and predicts for each person the probability of adverse effects from exposure. Moreover it is conducted at the site immediately.

The device though a bit cumbersome is still portable. The researchers say that their aim is to make the machine enable workers to be able to know quickly whether his respirator is working, his suit and gloves are not leaking, and his boots are intact. The machine may help the management to improve safety standards quickly. Workers can be screened at any short intervals of time depending on the individual requirement in different environments.

In addition to the above use, Batelle scientists are trying to exploit the potential of the machine as a diagnostic tool in the medical setting. The researchers hope to detect the VOCs by breath analysis to trace diseases like diabetes and cirrhosis of the liver which may ultimately serve as a quick method instead of laboratory analysis of blood.

Similar line of research conducted on rats is being explored by scientists at the Research Triangle Institute and the NIEHS in Research Triangle Park, North Carolina. The researchers have identified and quantified the hundred or so VOCS found in the expired breath of rats. These preliminary studies have shown that there were consistent differences in breath components in male and female rats, and these responded in predictable ways to changes in the sex hormone status of the animals.

After they are through with the studies on animals, the team would like to study the possibility of using their machine which can detect minute concentrations of VOCs, to apply such a breath analysis studies in the same way that blood tests now are used in the medical setting. This could be a simpler and more rapid means of identifying metabolic changes so that therapeutic measures could be applied quickly [*Env Health Persp*, **104**(12)(1996)1292-94].   ❑

DSRM

Spreading Hi-Tech coatings to small industry

The vapor deposition alloy coating process has progressively replaced chromium coating across a wide range of industrial and medical applications. It is widely used in aluminum press tools and plastic moulds. Demand for the utilization of this technique is exploding, but process costs have so far excluded small companies from this lucrative market, as specialist companies have sought to reduce their prices by building larger systems. The available systems operate mostly in batch mode. Deposition takes place in vacuum and the process is very slow. Typically, each cycle lasts five hours. For each batch of products, it takes around three hours to pump the deposition chamber down to the required pressure. Thus, bigger and bigger systems are used.

A new Innovation Project being undertaken by Manuel Braun of the Kungliga Tekniska Hogskolan (KTH) in Stockholm aims at the utilization of this technology for small scale in-house applications. The technique can then find usage to do the coatings in-house, incorporating the process into the production lines itself. In-house coating will be made cheaper and the transportation costs will be cut down. Smaller companies will gain access to the technology, enabling them to increase their current prices by improving the quality of their products.

The Innovation Project, which entered its 3-year demonstration phase in November 1996, aims at creating a small, fully automated coating system, capable of non-stop operation, reducing the length of the coating cycle by more than 90 per cent to around 20 minutes, and opening up the possibility of continuous production.

This will be achieved by maintaining the vacuum in the deposition chamber, avoiding lengthy pumping down between cycles. Racked products will be loaded into a primary chamber, whose pressure will be reduced as they are heated and cleaned. After less than 20 minutes, as soon as the previous cycle has been completed, valves will open to allow the new load to enter the deposition chamber, and the coated products to pass into a third chamber for cooling and unloading.

Planned deposition techniques are well known, and vacuum interlock systems are widely used in the semiconductor industry. The planned system's unique feature will be the high rate of throughput to be made possible by combining these two technologies.

KTH itself will develop and build the main chamber and the positioning unit, and will coordinate the project, while a Swedish firm will build the transport and interlock system. Sophisticated computer control will be developed by a small Dresden-based coating specialist so that unskilled operators can produce consistent, high-quality results. In the project's final phase, a second German company will conduct industrial tests on end-user applications. [*Innovation & Technology Transfer*, Vol.2 , March 1997, p.3].   ❑

CSG

Poison gas attacks leave fingerprints in blood

The lack of reliable tests for poison gas has been a major problem in banning the use of chemical weapons.

The chemical weapon poison gases are toxic, extremely reactive and decompose very quickly. Thus, it is hard to detect the poison gas in a victim's tissues.

Jan Peter Langenberg and coworkers of the Prins Maurits Laboratory for Military Research in Delft have carried out investigations involving the detection of stable compounds formed by poison gases with other compounds in the body. They have found that mustard gas forms stable compounds with DNA, and with proteins in blood. The longest-lasting compounds, formed with hemoglobin, can be detected with a simple immunoassay many months after the initial exposure.

Langenberg's work has already solved a 13-year-old mystery regarding the usage of chemical weapons during the Iran-Iraq war. Fifty Iranian soldiers were sent to Europe and Japan for treatment, following claims that they were the victims of gas attacks. Iraq, which has signed the chemical weapons treaty, denied using poison gas.

Knowing the type of gas that had been used was critical because the Soviet Union was accused of supplying mycotoxin chemical weapons to Iraq. But because of the delay in testing the victims no conclusive diagnosis could be made at that time. Different analyses by the Iranians implicated mycotoxins (yellow rain), nerve gas or mustard gas. Langenberg tested blood samples frozen at that time and proved that the soldiers were exposed to mustard gas.

Langenberg's test is reliable evidence of exposure to mustard gas. He is now looking for telltale signs of other chemical weapons. Organophosphorus nerve gases such as sarin, used in a terrorist attack on the Tokyo underground in 1995, block the enzyme which degrades the neurotransmitter acetylcholine. According to the scientist, sarin forms a stable compound with the enzyme which can be detected using a gas chromatograph. This method could be used on the battlefield to warn troops which chemical agent they were facing.

The technique could have applications beyond controlling chemical weapons. Organophosphorus pesticides such as malathion are chemically similar to nerve gases. Each year they kill many people in the Third World, as the victims do not realize what is causing their symptoms [*New Sci,* **153** (2075) (1997) 23]. ☐

CSG

New method to create buckymaterials

The chemists, K Peter C Vollhardt and Adam J Matzger, at the University of California, Berkeley, have found fullerenes in the form of layered onions and carbon nanotubes in the aftermath of an explosion of a high-energy organic molecule. This reaction could provide a new and general way to make the buckymaterials. The molecule, tetrabenzohexadehydro[20]annulene, synthesized by the scientists was intended as a possible intermediate for creating annulene-cross-linked polyenynes. This class of annulenes have few hydrogens and are considered high-energy because of their numerous triple bonds. After creating the molecule, the Berkeley team discovered that by simply heating it to 245°C under vacuum, it exploded with a spectacular orange colour flash, leaving a residue of black powder.

Solubility tests for fullerenes such as C_{60} and C_{70} initially turned up negative. However, further testing with transmission electron microscopy (TEM) revealed striking images of highly ordered structures: onions of up to 30 to 40 layers, both filled and hollow, and tubes with caps on the end, providing a new way of constructing buckymaterials.

The reaction yield was hard to quantify. In addition to the abundant, highly ordered carbon structures, plain graphite and amorphous carbon were also found.

Further investigations to control and optimize the reaction are necessary. Chemists interested in encapsulating potentially catalytic metals inside the onions and tubes for creating a highly protected environment allowing a molecule to enter, transform on a reactive metal, and come back out, may find the reaction useful [*Chem Eng News,* **75** (9) (1997) 11]. ☐

CSG

Spice oleoresins

Oleoresins from spices are the extracts of spices containing all the active flavoring principles of the original material and reproducing the character of the respective spices fully. The use of oleoresins is picking up well in the market because they provide standardized tastes in food and allied products. India and developing nations can benefit from the products as they can be produced from locally available spices at cheaper rates than in developed nations. They are largely used for food flavorings, particularly by large scale food and flavoring industries such as meat

canning, sauces, soft drinks, pharmaceutical preparations, perfumery, soap, tobacco, confectionery and bakery.

The process being offered by National Research Development Corporation (NRDC) gives oleoresins of international standards having solvent residues in oleoresins not more than 30 ppm. The process is amenable to small scale operation. Spices oils are distilled before being subjected to extraction so that the final product can be standardized easily. If good raw materials are used, spice oils will always be one of the co-products. The solvent meal obtained after removal of volatile and fixed oil can be dried and used in animal feed formulations. Spice oleoresins are concentrated extracts from the spices. They are obtained by solvent extraction of the powdered dried spices with subsequent removal of solvent. The volatile oil is distilled out from the ground spices. The wet powdered spices, free from volatiles, are dried and then extracted with suitable solvent systems to remove the fixed oil and resinous material. The solvent is removed from the miscella and dried and the extract is mixed with the dry spice oil to the required level, and the product is suitably packed.

Further details about the process may be obtained from: NRDC, Anusandhan Vikas, 20-22 Zamroodpur Community Center, Kailash Colony Extension, New Delhi, India-110048 [*Cordis Focus RTD- Results*, No. 13, 21st April 1997, p. 35].   ❑

CSG

Growing crystals with a twist

A chip has to be nearly defect free to give the best performance. But growing perfect crystals is difficult because of mismatches between the atomic lattice pattern of the semiconductor and the substrate, a supporting surface that provides a template for the crystal being deposited on top. As a result, strain builds up in the growing lattice, triggering cracks in the crystal. Now, the researchers from Cornell University in Ithaca, New York, and Sandia National Laboratory in Albuquerque, New Mexico, have reported that a thin, flexible film sandwiched between the substrate and the crystal can act as a buffer providing easy way to ease the strain. By absorbing the strain, it allows a wide variety of crystalline materials to be grown on the same substrate material virtually defect free, even when the distance between atoms in the two lattices differs by as much as 15 per

cent. These findings may allow the scientists to grow high- quality crystals of new semiconductors leading to the development of high performance computer chips as well as new optoelectronic devices.

The atoms in the substrates used to organize the growth of semiconductor crystals are locked into such a strong, rigid lattice that when strain builds up between the two layers, it is inevitably the more fragile, still-forming crystal that fractures. So, the scientists investigated the creation of a sacrificial layer that would absorb the building strain and fracture, thus sparing the growing crystal. This strategy was to top the substrate material with a few weakly bound layers of atoms that could move around and absorb the strain. But because any atoms deposited directly onto the substrate would be locked into the same rigid lattice, creating this weak layer required a little ingenuity. The team started with a slab of gallium arsenide (GaAs), a standard substrate crystal, coated with a layer of indium arsenide. A film of GaAs as little as five atomic layers thick was added which ultimately served as the flexible film. Finally, a second slab of GaAs was bonded on the top, but with a twist.

Instead of stacking the two slabs neatly, the scientists rotated the top GaAs slab so that its lattice was at a 45° angle relative to that of the substrate slab and the GaAs film, below. The researchers then used two conventional etching solutions to eat away the bottom two layers until only the ultrathin GaAs film was left attached to the second GaAs substrate. This served as the new substrate and starting material for growing high-quality crystals.

When the researchers tested their new substrate for growing new semiconductor compounds on top, such as one made from indium antimonide (InSb), the difference was readily apparent. InSb films grown on conventional substrates are normally riddled with as many as 10 billion defects per cm^2. But on the flexible substrate, the defects were reduced to an undetectable level.

According to the scientists, bonding the GaAs slab and ultrathin film together at an angle dramatically changes the property of the film by preventing the thin film's atoms from forming rigid covalent bonds with the bulk GaAs substrate. That allows the atoms in the thin layer to move absorbing strain.

Presently, there is no cheap substrate available with a lattice closely matched to gallium nitride (GaN). Thus, the grown GaN films contain billions of defects, which trap heat and cause the laser devices to burn out rapidly. The ability to grow relatively defect free semiconducting crystals could speed up the commercialization of blue lasers using semiconductor chips made from GaN [*Science*, **276** (1997) 356].

❑
CSG

One-step metal-mediated route to amino sugars

Chemists Erick M Carreira, Justin Du Bois, Craig S Tomooka, and Jason Hong, at the California Institute of Technology, have developed a reaction that provides rapid access to biologically important 2-amino sugars. They have used a metal complex to convert cyclic enol ethers, or glycals, into 2-amino sugars in one step. The reaction represents the first example of a metal- mediated glycal amination.

Earlier reactions to prepare 2-amino sugars usually involved several steps, yielding products in which the amine is protected by groups that typically are difficult to cleave.

The novel reagent used by the scientists is a manganese nitrido complex called (saltmen)Mn(N), prepared easily in one pot by reacting N,N'-(1,1,2,2,-tetramethyl) bis(salicylidene amino)ethane with manganese(II) acetate followed by treatment with ammonium hydroxide and Clorox bleach (sodium hypochlorite, NaOCl). In the presence of trifluoroacetic anhydride, the complex reacts with a glycal to produce a 2-amino sugar trifluoroacetamide.

The work was inspired by the pioneering glycal method of Samuel J Danishefsky, involving conversion of glycals to 2-hydroxy sugars, or to a 2-amino sugar sulfonamide from which a 2-amino sugar may be produced by hydrolytic or reductive cleavage.

The trifluoroacetamides are more user friendly because they are easier to cleave than sulfonamides. Carreira's team has shown that an intermediate in the reaction can be trapped with thiophenol to produce thiophenylated 2-amino sugars, which can be used as glycosylating agents. It may now be possible to trap the intermediate with another sugar to produce an amine disaccharide [*Chem Eng News*, **75** (15) (1997) 38].

❑
CSG

CO dissociation dynamics studied

Researchers at Harvard University have obtained femtosecond IR spectra of carbon monoxide dissociating from the heme prosthetic group in myoglobin, a protein that serves as a reserve oxygen source in muscle. The study enhances the sensitivity and time-resolution limits of IR spectroscopy, providing interpretation to the mechanism of CO dissociation under physiological conditions.

The work, carried out by Manho Lim, Timothy A Jackson and Philip A Anfinrud, demonstrates two routes by which CO can dissociate from heme and shows the role played by myoglobin conformational changes in the process.

Myoglobin's normal physiological function is to bind oxygen, but it is capable of binding other ligands like CO. Anfinrud and coworkers used a laser to photodissociate CO from myoglobin, obtaining the time-resolved IR spectra of the departing ligand. It was found that, upon dissociation of CO from its heme binding site, the ligand rotates about 90° and becomes trapped in one of two orientations at an adjacent docking site in the hydrophobic interior of myoglobin, a process that occurs in less than one picosecond. The docking site retains CO, preventing the ligand from reassociating with heme and giving it the opportunity to dissociate totally from the protein, which is a much slower process.

The studies show that CO takes one of two routes from its heme binding site to the protein docking site. In one case, it ends up at the docking site with its

CO dissociation from heme
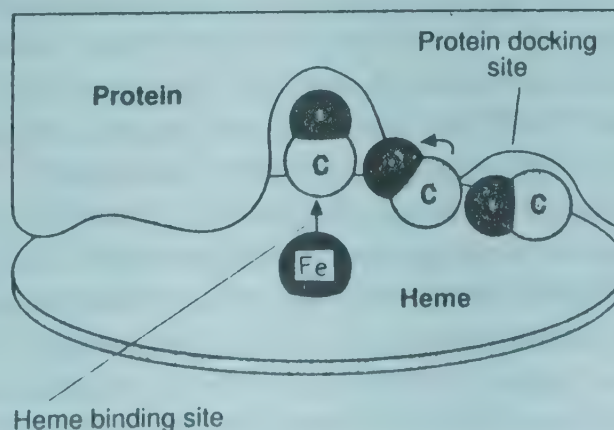
In one of two routes of CO dissociation from heme, the ligand rises from its binding site, rotates in a counterclockwise direction, and gets retained in a protein docking site in such a way that its carbon faces away from the heme center. In the other route (not shown), CO ends up in the opposite orientation.

carbon atom pointing away from the heme center. In the other, the carbon side points toward the heme center. As the ligand arrives at the docking site, the protein rearranges its local structure so that the reverse binding route of CO (back to heme) is effectively blocked. The researchers speculate that such a dissociation mechanism may also be relevant to other proteins whose activity requires the movement of oriented ligands to and from active sites.

The time resolution required to probe the rapid ligand and protein motions revealed in these studies is beyond the capability of current X-ray technology. Femtosecond IR spectroscopy, therefore, represents a powerful addition to the arsenal of tools currently available for probing the molecular origins of protein function [*Chem Eng News*, **75** (15) (1997) 38]. ❏

CSG

New catalysts

Richard Weiss *et al*. at the Georgetown University, Washington DC have found a technique to make gels that harden into porous materials. They have found several gelling agents, such as tetraoctyl-decylammonium bromide (TOAB), which can turn organic compounds into gelly.

Weiss and his colleagues mixed TOAB with a brew of either styrene, the building blocks of polystyrene, or methyl methacrylate, which is used to make Perspex. They added a polymerising agent, then heated the mixture until the solids dissolved. As the mixture cooled, the TOAB molecules formed a mesh, creating a gel. Further, they blasted it with UV light to trigger a polymerization reaction that made the gel solidify.

By heating the gel in an alcohol solvent, they were able to boil off the stringy TOAB molecules, leaving a solid material with μ-sized channels and pores where TOAB had been. In future, this kind of material could be used in the same way as zeolites.

To put the technique into industrial practice, it will require a lot of engineering. Unlike zeolites the new materials break down at high temperatures. But with more research, it is hoped to tailor the size and shape of the channels so that they can be put to use as low temperature "sieves" and catalysts in a wide range of reactions.

Martinus Feiters and his colleagues at the University of Nijmegen have developed a similar technique using compounds called gluconamides a gelling

TOAB gelling agent
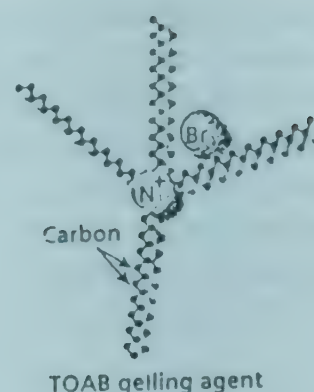
agents [*Chem Commun*, **No. 6** (1997) p. 543;545; *New Sci*, **154** (No. 2076) (1997) p. 20]. ❏

HKK

Tiny catalyst shows hidden talents

Leucine, one of the 20 amino acids from which nature constructs proteins, could serve as a cheap and environmental-friendly catalyst for industry when polymerised into short chains of between 15 and 30 leucine units to make polyleucine.

Stan Roberts and his colleagues at the University of Liverpool took an idea from earlier work of polyleucine's catalytic power. They have now proved that the amino acid excels at catalysing a chemical reaction called epoxidation, which inserts an oxygen atom into organic molecules at points where carbon atoms are connected by double bonds. The added oxygen atom forms a triangle with the two carbons.

They have catalysed around 100 reactions with polyleucine and have shown that it could provide a cheaper method for making diltiazem, a drug for treating angina.

Significantly, it was found that some epoxide molecules can be made in 'left-handed' shape or its 'right-handed' mirror image, simply by switching from left-handed polyleucine to the 'right-handed' form. This distinction can be important for drugs, as the two forms can have different effects in the body.

As polyleucine forms an insoluble goo, it can be filtered off afterwards and reused. It is speculated that polyleucine might have been one of nature's first catalysts, and may have helped to create the first sugars.

Roberts has shown that other polymerised amino acids, including polyalanine and polyvaline also serve as catalysts [*New Sci*, **154** (No. 2077) (1997). ❏

HKK

Cotton fibres engineered to make thermoplastic polymer

Maliyakal E John and Greg Keller at Agracetus, a unit of Monsanto, Middletown, Wisconsin, USA have engineered cotton fibres that express a natural thermoplastic polymer by introducing into cotton seed bacterial genes that code for enzymes involved in the synthesis of poly-hydroxy-burtyrate (PHB). The hybrid fibres have improved thermal properties, including slower rates of heat uptake and dissipation and higher heat capacities.

Bacteria synthesise PHB from acetyl coenzyme A in multistep process that requires three enzymes: β-keto- thiolase, aceto-acetyl coenzyme A reductase and poly-hydroxy- alkanoate syntheses. Cotton plants contain the starting material and thiolase, but lack the other two enzymes. To endow the plants with the missing pair of enzymes and to track their expression, John and Keller cloned the genes for the enzymes along with the gene for a marker protein.

To localise PHB synthesis, researchers included a cotton promoter that turns on the reductase gene only in the fibres. The chimeric clones were then coated onto gold microparticles and "shot" them into germinating cotton seeds, using particle bombardment technique. The device called a gene gun that fires the microparticles at high velocity toward the target tissue was used. When a particle lodges in a cell, the cell takes up the DNA by some unknown mechanism, leaving the gold particle alone. Actually, 5,000 to 10,000 germinating seeds are bombarded to produce 10 to 20 transgenic plants. The number looks small, but that is what one normally gets with this procedure. Plantlets that express the marker protein are grown to maturity.

Transformed plants pass along recombinant genes to their progeny. The cotton experiment netted eight transgenic plants carrying all the recombinant genes. Because PHB is synthesised in the hollow of the fibres, it does not interfere with the architecture of their cellulosic cell walls which retain their structural integrity as the growing fibres elongate. Confining synthesis of PHB to the fibre avoids the stunting effects on growth and seed production observed in a weed-like transgenic plant crossbred to synthesise PHB. So far, the team has produced only minute amount of engineered fibres, with just small improvement in thermal properties. But the recombinant feat represents an important step toward producing new-generation fibres for the textile industry, by showing it is feasible to imbue cotton fibres with new traits.

The work also validates the utility of particle bombardment in genetic engineering.   ❑

HKK

Fuel catalyst improves engine performance and reduces emission

Researchers at the Warren Spring Laboratory, the Environmental Technology Executive Agency of Britain's Department of Trade and Industry have tested and confirmed a catalyst in-line fuel treatment unit for both petrol-and diesel-powered engines which improve fuel flow, combustion and engine efficiency, and can save up to 15 per cent or more on fuel expenses.

The *Powermaker* catalyst from Powermakers Plus, also improves engine-power performance by up to 16 per cent and reduces harmful exhaust emissions by up to 51.9 per cent.

The catalyst, which can be fitted by a semi-skilled mechanic to any vehicle, private or commercial, does not damage an engine or its fuel system. In use, it will maintain or return the top half of any engine to a condition of peak cleanliness and maximum potential efficiency by the removal and elimination of carbon residues, thus providing the best conditions for maximum overall operating efficiency during the lifetime of the engine.

Substantially reduced amounts of the particulate content of harmful exhaust gases are eliminated into the atmosphere because of the improved molecular structure of the fuel, which enhances the combustion process.

After the catalyst has been used for 500 miles or more on a vehicle running on leaded fuel, unleaded fuel can then be used as tin is leached by the catalyst to provide protection for the valve seats of older engines. The unit will also increase the life of catalytic converters because of the reduced emissions. No additives are needed, and no maintenance is required.

Additional benefit claimed for the *Powermaker* is that it compensates for the degradation which can otherwise cause exhaust catalyst to fail statutory emission tests, as a result of any internal failure which may have arisen in normal service and possi-

bly have rendered an exhaust catalyst illegal, were it not for the addition of the unit.

For further information contact:
John Hill, Powermakers Plus Ltd, Croft
Business Park, Bromborough, Wirral, England
L62 3 RD.   ❑
                                                              HKK

Plastics recycling process that does not discriminate

Researchers at the Polymer Reclamation Centre, Northwestern University, Evanston, USA have found a way to recycle plastics without sorting.

The process uses a modified connotating twin screw extruder developed earlier by H Berstoff Maschinenbau of Hannover, Germany. Plastics are pulverized into particles ranging from 20 to 2,000 μ, by simultaneously applying a high shear and extensive cooling.

Pulverization mechanically ruptures the chemical bonds, generating free radicals for formation of *in situ* blocks of graft co- polymers. The powders are suitable for direct melt processing by all existing plastic conversion techniques, like rotational molding and compounding. The powder can be stored for reuse, so cooling is employed to avoid melting the mixture in the extruder.

Powder size is controlled by process conditions and screening. The process is expected to be competitive, since storing is eliminated and the process requires little energy. A commercial- scale equipment is being developed. In a similar way, researchers at the Mitsubishi Heavy Industries Company, Japan, have developed a low-cost recycling process for the used automobile bumpers, which are made up of polypropylene.

An economical novel process is a simpler way to remove paint, a necessary step to avoid contaminating the recycled plastics. Used vehicle bumpers are cut into flat pieces, or plates, of roughly 500 X 500 mm thickness, and heated to their softening temperature(~100°C). The plates are then fed between two pairs of rollers that are located in series in a paint-peeling machine.
                                                                ❑
                                                              HKK

Ethanol sensor measures beer's alcohol content online

Researchers at Fraunhofer-Gesellschaft, Munich, Germany have developed a handled sensor that measures ethanol concentrations in beer and other process streams in less than 5 min.

This is a key advantage in brewing 'alcohol-free' beers, as the fermentation is to be stopped when the alcohol level reaches the limit of 0.5 volume per cent, prescribed in Germany.

Presently available off-line enzymatic or chromatographic methods take up to 1h, by which time the alcohol level may have been exceeded.

The key to the device is that it uses a nonamperometric electrochemical technique. The method is accurate to within 0.1 volume per cent ethanol. Ongoing refinements will reduce measurement time to less than 1 min, and an in-fermenter version is being developed. First industrial use will be at a German brewery shortly.   ❑
                                                              HKK

Bacteria communication

More than 400 different kinds of bacteria live in our intestines forming a complex, microscopic ecosystem that helps us with everything from making and absorbing vitamins to digesting food. But, little is known about the interaction of this microscopic menagerie with our bodies.

Recently, Per Falk, Jeffrey Gordon and Lynn Bry at Washington University School of Medicine in St. Louis, have found that some of these bacteria may actually communicate their needs to our intestinal cells, causing the cells to churn out sugars that the bacteria then eat.

The scientists carried out their investigations using germ-free mice and found that the mice produced a carbohydrate that contained the sugar fucose. As the mice matured in the sterile environment, they stopped producing the sugar. But upon the addition of a particular member of the intestinal tract's normal bacterial society called *Bacteroides thetaiotaomicron*, which uses the fucose for food, the intestinal cells once again began manufacturing the sugar, apparently in response to an unknown chemical signal secreted by the bacteria.

The scientists mutated the same strain of bacteria so that they could no longer eat fucose and then introduced the mutants to a germ-free mouse. It was

found that the mouse did not make the sugar, despite the presence of the mutant bacteria.

The bacteria in human intestines are very similar to those found in mice, and prompt intestinal cells to release various sugars. Understanding the bacteria's needs is important because benign bacteria occupy ecological niches in our intestines that would otherwise be open to invasion from disease-causing germs. Once more is known about the intestinal bacteria, patients may be given bacteria capsules to help repopulate their intestines with friendly microbes [*Discover*, **18** (2) (1997) 23].   ❑
CSG

Malaria's sticky killer protein discovered

The discovery of the protein that makes malaria a potential killer has raised hopes for a new way of treating or preventing the disease. Scientists in Melbourne, Australia, have discovered how the parasite that causes cerebral malaria makes red blood cells stick to and clog capillaries in the brain. They have managed to stop cells sticking to mock human capillaries.

The parasite, *Plasmodium falciparum*, invades the red blood cells and produces proteins that form "knobs" on the cell surfaces. Some researchers have suggested that it is these knobs that make the blood cells stick to capillaries.

The team from the Walter and Eliza Hall Institute of Medical Research (WEHI), Monash University and the University of Melbourne decided to test this. They suspected that a protein called KAHRP (knob-associated and histidine-rich protein), which the parasite produces and which forms under the surface of the knobs, is essential for knob production.

To confirm this, the team used a technique called "gene knockout" to disrupt the gene that codes for KAHRP in parasitized blood cells. By adding an extra stretch of DNA to the gene, they blocked the production of the protein. Scanning electron microscopy later showed that knobs no longer formed on the cells.

To check whether it is the knobs that cause the blood cells to stick to capillary walls, the team mimicked the environment inside human capillaries using a slide covered with the capillary wall receptors that attach to parasitized blood cells. They passed unmodified parasitized cells with knobs and knobless "KAHRP-knockout" cells across the slide. The re-

searchers found that while the cells with knobs stuck, the cells without knobs flowed easily over the slide.

The researchers now plan to find out which parts of KAHRP are involved in knob formation. Eventually, this could lead to the possibility of making drugs that will block the function of KAHRP, and therefore block the formation of knobs. Further investigations may lead to the development of drugs for preventing malaria [*New Sci*, **154** (2081) (1997) 21].   ❑
CSG

Human cells make perfect proteins

A Protein that is used to treat anemia can now be manufactured in cultures of human cells, making it virtually identical to its natural counterpart. This technique has been developed by Transkaryotic Therapies (TKT) of Cambridge, Massachusetts.

All the synthetic proteins on sale at present including insulin for diabetics and human growth hormone are made by stitching copies of the human gene that makes the protein into non-human cells, such as those taken from the ovary of a Chinese hamster. These cells are then cultured. Non-human cells are used because they grow much better than human cells, and often produce much larger quantities of the protein. But because the human gene is at work in a foreign cell, the product that results can be subtly different from the natural human protein.

A human cell contains approximately 1,00,000 genes, but only a selected few are activated in each of the different cells in a living person. TKT has devised a way of switching on genes for producing proteins in cells where those genes would not normally be active.

Erythropoeitin, the protein that stimulates the production of red blood cells, is produced naturally only in kidney cells. The genes producing erythropoeitin are controlled by promoters, the genetic equivalent of on-off switches. Promoters sit next to the genes they control in segments of DNA called regulatory regions. The promoter for erythropoeitin production remains off in all cells of the body except kidney cells.

TKT's technique overrides the switch that is in the off position by providing an alternative artificial promoter. This allowed the TKT scientists to switch on erythropoeitin production in cells that would ordinarily never make it. To do this, TKT had to identify sequences of DNA unique to the regulatory

regions next to the gene making erythropoeitin. Having found the sequences, TKT fitted the artificial promoter with "homing tags", which guided it to a position in the vicinity of the gene. Once there, it bypassed the original promoter and the gene kicked into action for producing erythropoeitin.

The TKT technology can trick human cells into making a wide range of proteins by switching on the genes which produce the proteins in their natural surroundings. The company is confident that proteins made this way will be identical to those produced naturally, and as effective medically as those made in animal cells [*New Sci*, **154** (2080) (1997) 22]. ❑
                                                                        CSG

Treatment for tough tumours

Cancers that have been all but eradicated by conventional treatment often regrow into incurable tumours. The hardy cells that survive anticancer drugs and radiation often produce aggressive cancers. Now geneticists in Britain have hit upon a method of targeting these ultra-resistant cells.

Adrian Harris of the Institute of Molecular Medicine (IMM) in Oxford and his colleagues have developed a genetic switch that will start the production of a lethal protein in the 10 per cent of tumour cells that are ultra-resistant. The new technique could be used in conjunction with conventional treatments.

Because tumours grow and divide rapidly, they quickly exhaust local supplies of oxygen. Central regions of the tumour become oxygen-scarce, or hypoxic. Resistant tumour cells tend to develop in oxygen-deprived parts of the tumour. Under these hypoxic conditions, the new switch becomes activated.

The scientists have discovered the genetic switches called hypoxia-responsive elements (HREs), in segments of DNA known as regulatory genes. These genes are able to initiate or halt the reading of the structural genes that carry instructions for making proteins. The HREs only switch on protein production when oxygen levels are very low, *e.g.* during wound healing.

The researchers first confirmed that the switches are only triggered in hypoxic conditions, by attaching the HREs to structural genes that create a protein that can be detected on the surface of cells. They found the protein only in cells starved of oxygen. They then tested the same system in human cancers that had

been grown in mice. Once again, the switch only worked in regions of the tumour that were oxygen-starved.

These studies show clearly that the gene is switched on only in hypoxic regions. Investigations being carried out now involve attaching HRE to a protein that is toxic to the cancer cells in which it is produced, as well as neighboring caner cells, and use a retrovirus to introduce the artificial gene into tumour cells. That may create little protein factories in the tumour cells which are only switched on when the cells are hypoxic. The treatments based on these studies will have few side effects because oxygen starved regions are usually found only in tumours.

The gene therapy technique will attack secondary cancers as well as primary ones. In the next stage, the team is planning to test a version of the switch in women with breast cancer [*New Sci*, **154** (2081) (1997) 27].   ❑
                                                                        CSG

New vaccines for urinary tract infections

Urinary tract infections (UTIs) are caused primarily by *Escherichia coli*. Standard antibiotics usually offer quick relief. But UTIs recur frequently, and when untreated, cause kidney damage and even death. A vaccine could reduce this toll, but until now there has been little successful work in UTI vaccines.

The researchers at MedImmune, a Maryland based biotech company, and at Washington University in St. Louis have now developed a genetically engineered injectable vaccine that prevents UTIs in mice. These studies could result in reduction of the number of UTI cases.

The strategy followed by the scientists involves targeting a single protein that enables the bacteria to latch onto their target cells. It could prove to be valuable against other infections also.

Earlier efforts to combat UTI-causing microbes involve the usage of injectable cocktail of killed UTI-causing bugs, called Urovac, providing a short-lived protection. But natural toxins in the organisms often trigger painful inflammation around the injection site. To minimize inflammation, studies using the same concoction of killed organisms as in the Urovac vaccine, but relying on the vaginal suppository delivery method were carried out. It was hoped that by allowing killed microbes to diffuse through the entire vaginal tract instead of injecting them into

one small part of a muscle, a suppository would avert inflammation, and that the killed organisms would still trigger the production of a class of antibodies known as secretory IgA, which circulate in mucosal surfaces such as the lining of the urinary and reproductive tracts and block invading microbes. In preliminary trials of 25 women, the vaccine seemed at least partially effective. Women who were prone to UTIs acquired infections less readily, and none reported side effects. However, the vaccine's protective effect diminished over time meaning that women would have to be re-administered the vaccine, possibly as often as every few months.

The MedImmune-Washington University team, led by MedImmune's Solomon Langermann and Washington University's Scott Hultgren, used a vaccine that triggers the immune system to produce antibodies blocking the action of just a single key protein on UTI-causing microbes. Administering only that protein does away with the need to expose patients to the whole organisms and their side effects producing toxins. The researchers targeted an "adhesion" molecule called Filamentous H, or FimH, present on *E. coli*. The microbes deploy FimH on the end of long, spaghetti-like strands that extend from the cell body and latch onto sugar molecules on the surface of host cells. The blockage of that interaction results in the prevention of the infection.

Researchers have tried to develop adhesion vaccines for other diseases such as gonorrhea, which is caused by organisms that rely on adhesion proteins. When genetically engineered bacteria are coaxed into producing the large amounts of adhesion proteins needed for a vaccine, the proteins often become degraded or clumped together, losing their ability to provoke immune cells into making antibodies targeted to the protein.

So, the MedImmune-Washington University team whipped up two separate vaccine formulations in the hope that at least one would yield suitable proteins. For the first, the researchers genetically engineered *E. coli* to express extra FimH, which they then collected and purified. As in earlier efforts to develop adhesion vaccines, these proteins ended up partially degraded. But fortunately, the part of the protein that triggers a protective antibody response remained intact. In the second formulation, the scientists modified the bacteria to express not only FimH, but also

chaperone proteins, which ensure that proteins fold into their proper conformation as they are made.

The team injected separate groups of mice with the two vaccines and exposed them 9 weeks later to UTI-causing *E.coli*. Both groups of vaccinated mice were able to ward off UTIs for more than 7 months. Analyses of the animals' urine showed that both vaccines had elicited blood-circulating IgG antibodies, some of which leaked into the mucosal lining of the bladder and urinary tract. These antibodies were believed to be bound to *E. coli's* natural FimH proteins, preventing the bacteria from binding to their target cells.

Investigations to demonstrate that the vaccine can block UTI-causing *E. coli* in humans while sparing another colony of *E. coli*, the beneficial intestinal flora that keep disease-producing bugs from proliferating in the gut. The new adhesion vaccine's initial success could pave the way for developing a host of other such vaccines for other diseases [*Science*, **276** (1997) 33].   ❏

CSG

Failures in genetic testing found

A study done by physicians administering a genetic test for colon cancer has found serious failures in their understanding of the significance of the tests and their education of patients. Only 18.6 per cent of patients received counselling before testing, and 16.9 per cent gave written informed consent and more than 20 per cent did not meet accepted criteria for testing.

A team led by Francis M Giardiello of Johns Hopkins University, School of Medicine, Baltimore, Maryland, studied 177 patients who were tested for the gene for *adenomatous polyposis coli*, an autosomal dominant disorder that causes cancer unless the colon is removed. In their conclusion they found that doctors misinterpreted the test results in 31.6 per cent of cases [*Nature*, **386** (1997) p. 317; *The New Engl J Med*, (1997) pp 336, 823-827].   ❏

HKK

Honours and Awards

Sir John Maddox wins Cultural Award

The Eward Rhein Foundation 1997 Cultural Award has been given to Sir John Maddox, the former editor of Nature, in recognition of his long-

standing commitment to furthering and disseminating scientific knowledge as the editor of *Nature*. The foundation was set up in 1976 and is named after the German writer and inventor Edward Rhein who died in 1993. The awards are given to promote scientific research in arts and culture. The winner of the award gets $ 130,000.

Rangaswamy Srinivasan to receive Esselen Award

The American Chemical Society's Northeastern Section has named Rangaswamy Srinivasan the 1997 recipient of its Gustavus John Esselen Award. The award recognizes a chemist whose scientific and technical work has contributed to the public well-being and has thereby communicated positive values of the chemical profession. Significance of the work should have become apparent within five years preceding nomination.

Srinivasan, president of UVTech Associates, Ossining, N.Y is cited for his discovery of the phenomenon of ablative photo decomposition (APD) and for his creative application of this technique to the patterning and micro-machining of polymers and biological tissue.

Srinivasan received B.Sc. and M.Sc. degrees from the University of Madras, India, in 1949 and 1950, respectively, in 1956, he received a Ph.D. degree in physical chemistry from the University of Southern California. After two postdoctoral fellowships, he joined the research staff at IBM's T.J. Watson Research Center in York Town Heights, N.Y., in 1961; he retired from there in 1990. He holds 21 patents [*Chem & Eng News*, March 10, 1997, p. 55].   □
                                                        DSRM

Report of the Working Groups of Information Society Forum of the European Commission

The European Commission decided to set up the Information Society Forum in February 1995 in order to create a new and authoritative source of reflection, debate and advice on the challenges of the Information Society.

The Forum consists of 128 members drawn from five main fields of activity:

* Users of the new technologies: industry (banks' retail, maritime etc), public services, consumer groups, small and medium-sized enterprises and the professions

* Social groups: academics, employers organisations and trade unions, youth groups, regional and city representatives

* Content and service providers: publishers and authors, film and TV producers, broadcasters, computer software producers and information service providers

* Network operators: fixed telecommunications, cable TV, mobile and satellite operators

* Institutions: members of Parliament, of the Economic and Social Committee of the Committee of the Regions and the data protection Commissioner.

Six working groups have been formed whose members have given their views under the following heads:

* the impact on the economy and employment;

* basic social and democratic values in the "virtual community,"

* the influence on public services

* education, training and learning in the Information Society

* the cultural dimension and the future of the media

* sustainable development, technology and infrastructure

The European Commission has published the first Annual Report and the supplementary report (working group's reports) which can be obtained from the Information Society Forum Secretariat (European Commission, Information Society Activity Centre, 200 Rue de la Loi, BU 24, 2/70, B-1049 Brussels. The full texts are also available on the ISPO web server at: URL: http:/vww. ispo. cec be/info-forurm/pub.html

Summary of the report of Working Group IV under the head "Education, Training and Learning in the Information Society" is given in this issue. The other reports of the Working Groups will be covered in subsequent numbers of JSIR one in each issue.

Summary of Report of the Working Group IV: Education, Training and Learning in the Information Society

Statements

1.The economic and social importance of Lifelong learning

The Information society will depend heavily on the Lifelong Learning infrastructure, both for its economics viability and its social resilience to the

stresses induced by continuous change. Lifelong learning involves skills and knowledge of three kinds[1]:

*General education attainment: this refers to educational standards and knowledge which enable people to function effectively in a wide variety of economic and social contexts; In the Information Society, it includes IT and network literacy.

*Job-specific skills: these are skills that tend to be of value only to people doing particular jobs with particular employers.

*Transferable vocational skills: these are skills relevant to particular jobs, which have uses in other jobs or with employers elsewhere.

We must aim to create an Education, Training & Learning environment in which the contributions made by educational institutions, firms, home and other organisations build productively on each other to achieve Life Long Learning. The potential role of Information and Communication Technology (ICT) in facilitating such development is significant. Significant innovative experiments have shown the potential of ICT to improve the learning process. However, supporting sustainable in our education systems will not be easy!

2.IT in school means changing Schools

The debate about the Information Society (IS) often significantly underestimates the huge amount of effort, time and money needed to achieve necessary change across the whole education sector, especially in the compulsory school sector, It is hard to imagine how the school sector's practice is going to evolve rapidly enough to cope with the changing fabric of society and expectations of young people. The sheer scale and traditional inertia of this sector has to be understood from within - and not just by external observers who are not part of the process. Any IS forum initiatives must rest firmly on actions rooted in "real world" situations in communities across Europe.

By Comparison, Further & Higher Education institutions are well positioned to take advantage of new opportunities and are, on the whole, already making substantial changes to allow them to do it.

These institutions may well be the main drivers for change in the Learning Community environments and so it remains important to keep them inside the development loop for any initiatives in the future.

3.Enterprises as a place of instruction and learning must be recognised .

As the White Paper "Teaching and Learning: Towards The Learning Society" stresses companies have an important role to play in the teaching and learning process, especially through alternating form of training. Companies, in particular SMEs, have to continuously detect and remedy their expertise gaps to improve their competitiveness.

4.The cycle of "barriers to progress" to good practice in Education, Training & Learning

*Schools and colleges don't have enough technology (computers, networks and multimedia facilities) in order for the institutions to see their use as "mainstream" and so to plan strategically to use them meaningfully.

*We face a huge challenge if we are to give teachers and trainers new tutorial skills in order for them to take advantage of such technology facilities even if they should become available.

*Even if the technology facilities and the teachers' skill levels were appropriate to the needs, we don't have adequate software and courseware appropriate to the school and college curriculum. Moreover, there are few signs that the quality, procurement and education-industry partnership issues that might solve this famine are yet being seriously addressed.

*The European and member states' approaches to deregulation of the telecommunications industry are a significant factor in the possibilities that are available to educators to pick up new approaches to supporting learning and so help create a genuine market place for the future.

Main issues

*The future of education, training & learning is one in which the public school sector will increasingly need to participate in a partnership with private sector parties. In order to ease the transition to the Global Information society schools and colleges will need to pursue a more community-focussed and business-focussed role in the provision of facilities and learning opportunities to all members of the community, many of whom will not be able to afford access to the high-technology resources required or will have individual needs for which access to ICT is of particular benefit.

*Private sector firms to fuel the development of multimedia software items is huge and our schools and colleges could enormously benefit from having the wide range of archive materials made more freely available to support a linguistically and culturally diverse range of curriculum developments.

*A fundamental barrier to development of good practice in this area is the widely recognised need to support teachers and other educators take advantage of Information & Learning Technology by the development of new teaching and learning strategies, taking account of the necessary shift from teacher-centredness to learner-centredness.

*Experience suggests that the delegation of an increased level of financial and managerial authority to school and college managers greatly assists the flexibility of the education system to cater for such community need. [First Annual Report to the European Commission from the Information Society Forum Secretariat, European Commission, Information Society Activity Centre, 200 Rue de la Loi, BU 24, 2/70, B-1049 Brussels].

Journal of Scientific & Industrial Research
(Incorporating *Research and Industry*)
Instructions to Contributors

The **Journal of Scientific & Industrial Research** (Incorporating *Research and Industry*) is published monthly to serve as an information link between the generators and users of technologies. It is addressed primarily to industrial entrepreneurs, technologists, engineers, technocrats and administrators in industry. Therefore, original research articles of practical interest to industry are invited for publication.

Contributions should have an economic bias, and wherever possible, cost estimates should be provided. They should be tersely written, giving only the significant results.

Besides, reviews on various branches of science and technology, science/industrial policy and management are also accepted.

Subject Coverage

Scientific Industrial Research

(i) Scientific investigations successful at the pilot-plant and in-plant trials.

(ii) Technology upgradation.

(iii) Development of cheaper and indigenous raw materials as replacement for uneconomical materials.

(iiv) Import substitution.

(v) Technologies for rural development.

(vi) Standardization and quality control.

(vii) Technologies of waste management.

(viii) Industrial R&D highlights.

Technology Management

(i) Success/failure stories in technology management.

(ii) Technology assessment.

(iii) Technology transfer.

(iv) Technology assimilation and adaption in different industries.

(v) Technology funding including venture capital.

(vi) Human Resource Development.

vii) Management.

(viii) Environmental management.

Industrial Development

(i) Policies, programmes and progress.

(ii) Critical profiles of industries—individual and sectoral.

(iii) Technology Forecasting .

(iv) International Collaboration.

(v) Fiscal incentives aimed at industrial development.

Books, monographs and technical bulletins on industrial methods and techniques as well as other data like production and demand statistics are accepted for review.

A critical analysis of papers presented at any Indian as well as international technology seminar/symposium is also welcome.

Questions on the articles published in the journal, answers supplementing any of the published items, views, opinions, or suggestions on the various aspects of technology are welcome for inclusion in the column, 'readers react'.

The editors are keen in projecting the technology bottlenecks/problems faced by the industry for their solution by the scientists in various laboratories. They would welcome to be mediators between the industry and the laboratory.

Preparation of Manuscript

Manuscripts should be presented in electronic form as well as in hard copy. Pages should be numbered consecutively, and the matter should be arranged in the following order: title; name(s) of author(s); department(s) and institution(s); abstract; keywords; introduction; materials and methods; results and discussion; acknowledgement; and references. The abstract, tables and captions (for figures) should be typed on separate pages.

The electronic form of the manuscript should be submitted on a floppy disk of 5¼" (1.2 MB) or 3½ (1.44 MB) to the Editor along with one hardcopy print out and one xerox copy. Text of the manuscript may be entered using word processing softwares such as Word Perfect Version 5.5/6 or MS Word Version 6 (preferably on IBM compatibles) and for illustrations Corel Draw, Harvard Graphics or any compatible format software (BMP, GIF, JPG, PCX, TIF) may be used. Label the floppy disk with the author(s)' name(s), the word processing package, software for illustrations, and the type of computer. In case of discrepancy between the disk and the manuscript, the latter will be taken as the definitive version.

Title—The title, not exceeding about 50 characters, should be such as to be useful in indexing and information retrieval. If a paper forms part of a series, a subtitle indicating the aspect of the work covered in the paper should be provided. If the title is long, a short title suitable for use as running title should be supplied.

Name and Address—The names of all the authors with initials, if any, should be given along with the name(s) of institution where the work has been carried out. The present address of authors(s), if different from the place of work, should be given as footnote(s).

Abstract—The abstract, usually not exceeding 200 words, should indicate the scope and method used in the paper, highlighting the principal findings and conclusions

Graphical Abstract—A short graphical abstract to be included in contents pages should also be submitted

Keywords—Five to six in alphabetical order should be provided.

Introduction—The introductory part should be brief and state precisely the scope of the paper. Literature review should not exceed what is necessary to indicate the objectives of the research undertaken and the essential background.

Materials and Methods—New methods should be described in sufficient detail, but if the methods are already well known, a mere reference to them will do; deviations, if any; should however be stated.

Results and Discussion—Only such data as are essential for understanding the discussion and main conclusions emerging from the study should be included. Data should be arranged in a unified and coherent sequence so that the report develops clearly and logically. The data should be statistically analyzed, and the level of significance given. The same data should not be presented in both tabular and graphic forms.

The discussion should deal with the interpretation of results. It should relate the new findings to the known, and include logical deductions.

Acknowledgement—This should be brief and for special assistance only, not for routine 'permission' to publish, or such trivial formalities.

References—References to literature, numbered consecutively, should be placed at the end of the paper. In the text, they should be indicated by numbers placed above the line (superscript).

In citing *references to research papers*, names and initials of the authors should be followed, in order, by the title of the periodical in the abbreviated form (italics), the volume number (bold), the year within circular brackets and the first page reference .e.g. Liotta R, Rose K & Hippo`E. *J Org Chem.* **46** (1981) 227

For names of periodicals, the standard abbreviations listed in the *International Serials Catalogue* published by the International Council of Scientific Union`s Abstracting Board should be used If the reference is to an article published without any

authorship in a periodical, the title of the artilce takes the place of the author in the citation, e.g. Handloom Sector of Textile Industry in India, *J Mater Sci*, **18** (1983) 1443.

If a paper has been accepted for publication, the names and initials of the authors and the journal title should be given followed by the words "in press" within circular brackets, e.g. Chavan R B & Subramanian A, *J Sci Ind Res*, (in press).

Reference to a book should include, names and initials of authors, the title of the book (italics), name of publisher and place of publication within circular brackets, year and the particular page reference, e.g. Hearle J W S & Peters R H, *Fibre Structure* (The Textile Institute, Manchester) 1963, 91. If the reference is to the work of an author published in a book by a different author or edited by a different person, the fact that is cited from the source book (italics) should be clearly indicated, e.g. Karr C (Jr), cited in *Analytical Methods for Coal and Coke Products* by Karr C (Jr) (Academic Press, New York, London) **Vol. 1**, 1978, 7.

Proceedings of Conferences and Symposia should be treated in the same manner as books. Reference to a paper presented at a conference, the proceedings of which are not published, should include, in the following order, the names and initials of the authors, title of the paper (italics), title of the conference, place where the conference was held, and date, e.g. Rao N V, Murty G S, Rao H S & Lahiri A, *Proceedings of the Symposium Chemicals and Oil from Coal* (Central Fuel Research Institute, Dhanbad, India) 6-8 December 1960, pp. 512-516.

Reference to a thesis should include the name of the author, title of the thesis (italics), university or institution to which it was submitted, and year of submission, e.g. Ghosh G, *Ph D Thesis, Structure of Coal*, Jadavpur University, Calcutta, India, 1984.

Reference to a patent should include names of patentees, country of origin (italics) and patent number, the organization to which the patent has been assigned within circular brackets, date of acceptance of the patent and reference to an abstracting periodical where available, e.g. Trepagnier J H, *U S Pat* 2,463,219 (to *E I du Pont de Nemours & Co.*) 1 March 1949; *Chem Abstr*, **43** (1949) 7258.

Even if a reference contains more than two authors, the names of all the authors should be given. The abbreviations *et al., idem and ibid* should be avoided.

Unpublished papers and personal communications should not be listed under reference but should be indicated in the text, e.g. Khanna V K, Unpublished work/data); (Kashyap K, Personal communication).

Tables— These should be typed on separate sheets of paper without any text matter. They should be numbered consecutively in Arabic numerals and should bear brief titles. Column headings should be brief. Units of measurement should be abbreviated and placed below the headings. Negative result should be indicated as 'nil' and absence of data by a dash. Inclusion of structural formulae inside the tables should be avoided.

Illustrations—Two stes of illustrations are to be submitted. These must be numbered consecutively in Arabic numerals. Captions and legands to the figures should be self-explanatory and should be typed on a separate sheet of paper and attached at the end of the manuscript. Line drawings should be made on white drawing paper (preferably Bristol board) or cellophane sheet.

Micrographs should include bench marks. Special care should be taken with computer listings, which are often not suitable for reproduction. In the case of photographs, prints must be on glossy paper and must show good contrast. If an illustrations is taken from another publication, reference to the source should be given and prior permission secured. Illustrations should be referred to in the text by numbers.

For satisfactory reproduction, the graphs and line drawings should be drawn to about twice the printed size. **The size of letters, numbers, dots, lines, etc. should be sufficiently large (5mm) to permit reduction to the page (165mm) and for the column (80mm) width, as** required in the journal, without loss of detail.

Footnotes—These should be avoided as far as possible Essential footnotes may, however, be indicated by superscribed alphabets a,b,c.

Structural Formulae—The number of structural formulae should be restricted to the bare minimum. Wherever the purpose is adequately served by giving chemical or common names, these should be preferred.

Abbreviations and Symbols—Standard abbreviations should be used in the text, tables and illustrations without full stop.

SI Units—SI must be used for units for all numerical data. Common metric (cgs), engineering, or other frequently used units may be given in parentheses following the Si units.

Proofs—Page proofs will normally be sent to authors.

General—Notations *and* meaning of symbols should be defined. Use of all capital letters such as 'MANUSCRIPT' should be avoided. The word per cent should be written in full as two separate words and not as %.

MANUSCRIPT NOT CONFORMING TO THE ABOVE GUIDELINES WILL NOT BE ENTERTAINED.

BOOKS

on

PHARMACEUTICAL & MEDICAL SCIENCES

from

NISCOM

	Price (Rs.)	Postage (Rs.)
* The Treatise on Indian Medicinal Plants		
Vol.-I	250.00	10.00
Vol.-Ii	300.00	10.00
Vol.-III	350.00	15.00
Vol.-IV	400.00	15.00
* Compendium of Indian Medicinal Plants		
Vol.-I	300.00	15.00
Vol.-II	550.00	15.00
Vol.-III	600.00	15.00
Vol.-IV	750.00	15.00
* Glossary of Indian Medicinal Plants	180.00	10.00
* Supplement to Glossary of Indian MedicinalPlants	80.00	10.00
* Second Suplement to Glossary of Indian Medicinal Plants	160.00	12.00
* Status Report on Cultivation of Medicinal Plants in NAM Countries	300.00	15.00
* Status Report on Aromatic and Essential Oil-bearing Plants in NAM Countries	400.00	15.00
* Medicinal Plants: Bibliography of CSIR Countributions (1950-1987)	60.00	10.00
* Heal with Herbs	50.00	3.00
* The useful Plants of India	300.00	15.00
* A Dictionary of the Flowering Plants in India	63.00	10.00
* Drug Addiction with special reference to India	50.00	10.00
* Tropical Diseases	600.00	20.00
* Medicinal & Aromatic Plants Abstracts (International Journal) Annual Subscription	500.00	-
* The Wealth of India (Raw Materials) (XI Vols. with 3 supplements)	4070.00	-
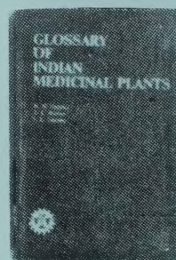
Order should be accompanied by Demand Draft/Money Order/IPO made payable to **National Institute of Science Communication, New Delhi** and sent to:

Sales & Distribution Officer
National Institute of Science Communication, CSIR
Dr K.S. Krishnan Marg, New Delhi 110012
Phones:5785359, 5786301/7 Ext 287,288
Gram:PUBLIFORM , Telex:031-77271, Fax:011-5787062